

**STUDIES OF SOME SYNTHETIC
ASPECTS OF
NON-STABILIZED AND STABILIZED SULFURANES**

A THESIS
for the Degree of
DOCTOR OF PHILOSOPHY
in
CHEMISTRY

**Submitted to
BUNDELKHAND UNIVERSITY
JHANSI
1993**

By
SANJEEV GUPTA
M. Sc.

Supervised by
Dr. K. C. GUPTA
M. Sc. Ph. D.



**DEPARTMENT OF CHEMISTRY
DAYANAND VEDIC POST GRADUATE COLLEGE
ORAI (U. P.) INDIA**

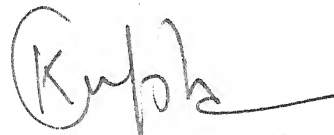
DEDICATED TO
My
PARENTS

CERTIFICATE

Certified that the thesis entitled
"STUDIES OF SOME SYNTHETIC ASPECTS OF NON
STABILIZED AND STABILIZED SULFURANES", by
Mr. Sanjeev Gupta, embodies the work carried
out by him under my supervision. The work
reported in the thesis is all original and
has not been submitted elsewhere for the
award of a degree Mr. Gupta has put in more
than 200 days attendance in the laboratory
during this work.

PLACE: ORAI

DATE : 30 JULY, 93


(DR. K.C. GUPTA)
Department of Chemistry
D.V. (P.G.) College
ORAI (U.P.)

ACKNOWLEDGEMENT

I deem it a pleasant duty and proud privilege to place on record my deepest sense of indebtedness to Dr. K.C. Gupta (M.Sc., Ph.D., F.I.C.S.) for introducing me to the field of ylides Chemistry and for his stimulating guidance and kind supervision throughout the course of this investigation.

I will be failing in my duty if I do not express my deep sense of gratitude to Dr. S.P. Saxena, Head, Chemistry Department of D.V.(P.G.) College, Orai for his inspiration, kind help and invaluable suggestions during the progress of my research work.

I wish to acknowledge my thanks to my teachers, Drs. A.K. Nigam, I.M. Beg, J.P. Pachauria, S.P. Srivastava, G.S. Niranjana, R.K. Nigam, S.K. Gupta, R.L. Viswarkarma and Mr. A.K. Srivastava for their encouragement.

I am also indebted to my colleagues, Messrs, Dr. P.K. Pathak, Dr. B.K. Saxena, Dr. A.K. Gupta, Dr. R.K. Gupta, Dr. U.C. Mishra, Dr. B.P. Pushpkar, Mr. Inayat Ali, Mr. Mohd. Masroor Beg for their active help during the course of this investigation.

My sincere thanks are due to Dr. G.S. Niranjana, Principal D.V.(P.G.) College, Orai for his encouragement and provision of laboratories facilities.

I am also thankful to the Director of C.D.R.I. Lucknow for providing facilities of spectral studies on a number of compounds.

I will always remain grateful to my elder Brother Mr. Rajeev Gupta, M.Tech., IIT Kanpur and loving younger sister Dr. Km.Rashmi Gupta, M.B.B.S. for giving their encourageful cooperation for completing my reaserch work.

I shall always obliged by Mr. Rajesh Kumar Gupta my colleage for making efficient typing of this thesis.

At last but not the least, I take the opportunity of expressing my deep gratitude to my parents to their encouragement and blessings at each & every stage of my carrier. Their kindness & understanding enabled me to traverse this difficult path, without their inspiration this present piece of work would have been quite impossible.

PLACE: ORAI


(SANJEEV GUPTA)

DATE : 1 Aug., 1993.

CONTENTS

| | | |
|-------------|---|-----------|
| | CERTIFICATE | i |
| | ACKNOWLEDGEMENT | ii |
| | PREFACE | iv |
| CHAPTER-I | Studies on some synthetic aspects of non stabilized and stabilized sulfuranes. | 01 - 43 |
| CHAPTER-II | Synthesis of 1,3,5-trisubstituted naphthalenes using non stabilized π -sulfuranes: Reaction of O-substituted benzyl dimethyl sulfonium bromides with α, β unsaturated ketones. | 44 - 77 |
| CHAPTER-III | Synthesis of some new 2,4,6-triaryl substituted pyridines: Using stabilized π -sulfuranes: Reaction of 4-methoxyphenacyldimethyl sulfonium ylide with α, β -unsaturated ketones. | 78 - 106 |
| CHAPTER-IV | Synthesis of 2,4,6-trisubstituted phenyl pyrimidines using 4-nitro phenacyldimethyl sulfurane and 4-fluorophenacyldimethyl sulfurane with aromatic aldehydes. | 107 - 132 |
| CHAPTER-V | Studies on metallation of p-substituted phenacylidenedimethyl sulfuranes: Hg(II), Cd(II), Co(II) and Ni(II) complexes of ambidentate sulfuranes. | 133 - 154 |

* * * * *

P R E F A C E

The thesis entitled "STUDIES OF SOME SYNTHETIC ASPECTS OF NON STABILIZED AND STABILIZED SULFURANES" has been divided into five chapters and each chapter describes specific aspects of ylide chemistry.

In chapter I, an exhaustive literature survey on π -sulfuranes leading to vast description about the types of non stabilized and stabilized sulfuranes. The chapter also contains the methods of preparation of stabilized and non stabilized sulfuranes and their some various important reaction.

Chapter II describes the reaction of benzyldimethyl sulfonium bromide and 4-nitrobenzyldimethylsulfonium bromide, 4-fluorobenzyldimethylsulfonium bromide, 4-bromodimethylsulfonium bromide with α, β -unsaturated ketones in presence of anhydrous $AlCl_3$ or $ZnCl_2$ at $150^\circ C - 200^\circ C$ which is used for cyclization agent. The structures of these naphthalene derivatives were confirmed by the elemental, IR and NMR spectral analysis.

In the chapter III gives an account of synthesis of new 2,4,6-triaryl substituted pyridines by the interaction of some 4-methoxyphenacyldimethylsulfonium bromide with α, β -unsaturated ketones in presence of a mixture of ammonium acetate and acetic acid. The structures of pyridines were confirmed by elemental, IR and NMR data.

In the chapter IV, various 2,4,6-tri substituted phenyl pyrimidines have been synthesized by the interaction of 4-nitrophenacyldimethylsulfurane and 4-fluorophenacyldimethyl sulfurane with aromatic aldehydes in presence of ammonium acetate and glacial acetic acid. Ammonium acetate in glacial acetic acid was used as aza cyclization agent.

The reaction takes place through Mannich type reaction. The methylene group of salt with aromatic aldehydes in presence of ammonium acetate forms Mannich base. Sulfonium salt which in turn, undergoes condensation with another molecule of benzaldehyde in presence of ammonia to form sulfonium salt intermediate. The later, then undergoes elimination of dimethylsulfoniumhydrobromide to form 2,4,6-triarylpyrimidines.

Chapter V, includes the studies on metallation of six p-substituted phenacylidene dimethylsulfurane with HgCl_2 , HgBr_2 , CdCl_2 , CoCl_2 and NiCl_2 . The ylide carbanion coordinates with metal ions which is confirmed by C=O stretching vibrations of complexes. The structure of complexes were evidenced by IR spectral data and elemental analysis.

* * * * *

CHAPTER I

CHAPTER - I

STUDIES OF SOME SYNTHETIC ASPECTS OF NON STABILIZED AND STABILIZED SULFURANES

A GENERAL SURVEY :

Ylide (1) are a new and unique class of zwitterionic compound in which carbanion is covalently linked to a positively charged heteroatom. Its structure is considered resonance hybrid of two limiting structures - Ylide forms (1a) and ylene form (1b). One of these, the ylide form (1a) emphasizes the dipolar zwitterionic nature involving an onium centre at elements like nitrogen, phosphorous or arsenic, next to a carbanionic function which may at least be partially delocalized into suitable substituents. In the ylene form (1b), on the other hand, a true double bond is postulated between the centre and ylidic carbon, thus reducing or even eliminating the formal charges at these atoms¹⁻². The application of modern physical techniques and the results of sophisticated theoretical calculations³⁻⁵, have made it increasingly clear that the ylide form predominates in the ground state. Most of the early investigations successfully used description for most of their problems of structure and reactivity and for the rationalization of reaction mechanism²⁻⁶. Therefore, it is with justification that the term ylide is used now a days almost exclusively in the literature.

The reactivity of the ylides depends both upon the

properties of the carbanion and on the possible involvement of the heteroatom. These compounds vary widely in stability, depending upon the symmetry of the molecule and the extent of $p_{\pi} - d_{\pi}$ bonding.

A quantitative comparison of the stability of ylides, formed by different elements, have been made using the rates of alkali catalyzed exchange⁷ of the α -hydrogen atoms of the corresponding salts. The acidity of salt and hence the stability of the ylide is greatly affected by the change in structure.

Ylide have been classified in two main groups on the basis of stability and ease with which they undergo reaction with a variety of electrophilic substrates. The first and the larger group comprises of ylides, called "non-stabilized ylides". Which are generated in the solution from their corresponding salts but could not be isolated due to the stabilizing factors and undergo reaction in situ. These ylides may further be divided in two categories depending upon the attachment of alkyl or arylalkyl groups with the heteroatom. The arylalkylidene ylides, sometimes designated as semi-stabilized ylides which could not be isolated but persisted in solution for a considerable time, in contrast to the alkylidene ylides which are very short-lived. The second and the smaller group consists of "stabilized ylides"

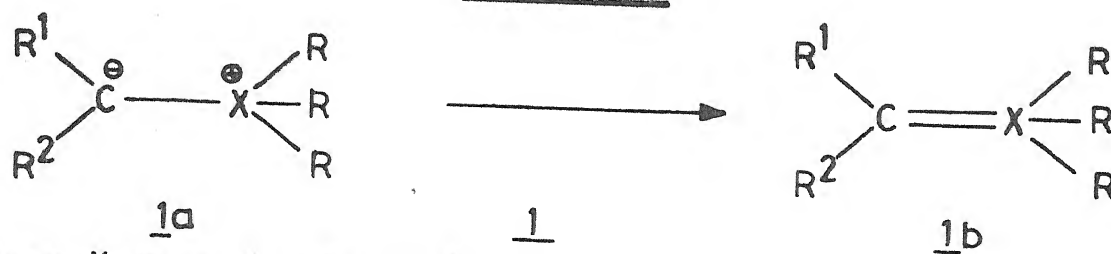
and is taken to imply an ylide which can be isolated, purified, usually stored in atmosphere and used in subsequent reactions. The stability of these ylides is attributed to the attachment of the electron withdrawing groups with the ylidic carbanion. In the recent years, the synthetic potentialities of ylides have been realized and studies on these reactive intermediates have been expanded in many directions which lead to the exploration of the ylides of nitrogen, phosphorous, arsenic and sulfur as evidenced by the research monographs^{6-11, 8-12} and comprehensive review articles¹²⁻²⁵. The involvement of a particular heteroatom results into marked difference in the chemical and physical behaviour of different types of ylides.

The scope and potential for synthetic applications of these ylides has only recently been realized. Consequently, studies on pyridinium, phosphonium, arsonium and sulfonium ylides and their corresponding precursors have been very extensive. These investigations have lead to the synthesis of a wide variety of heterolytic compounds, vitamins, hormones etc. as evidenced by a large number of monographs⁶⁻¹¹ and comprehensive review articles¹²⁻²⁵. A brief description under separate heads has been reviewed in the following section.

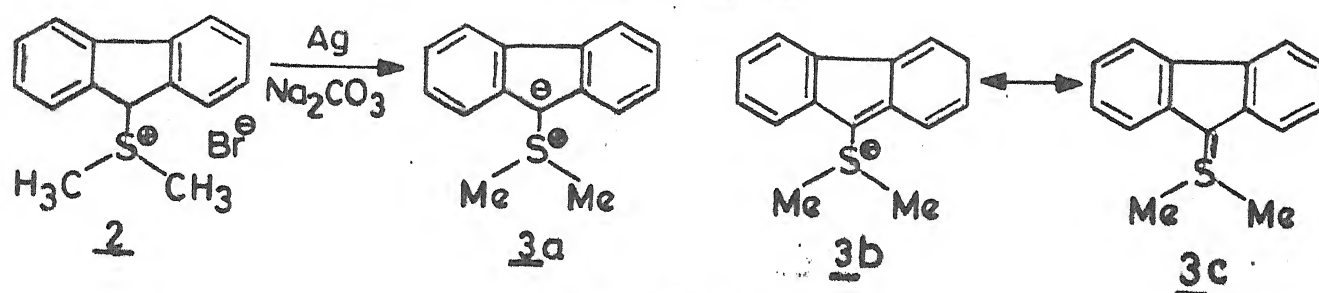
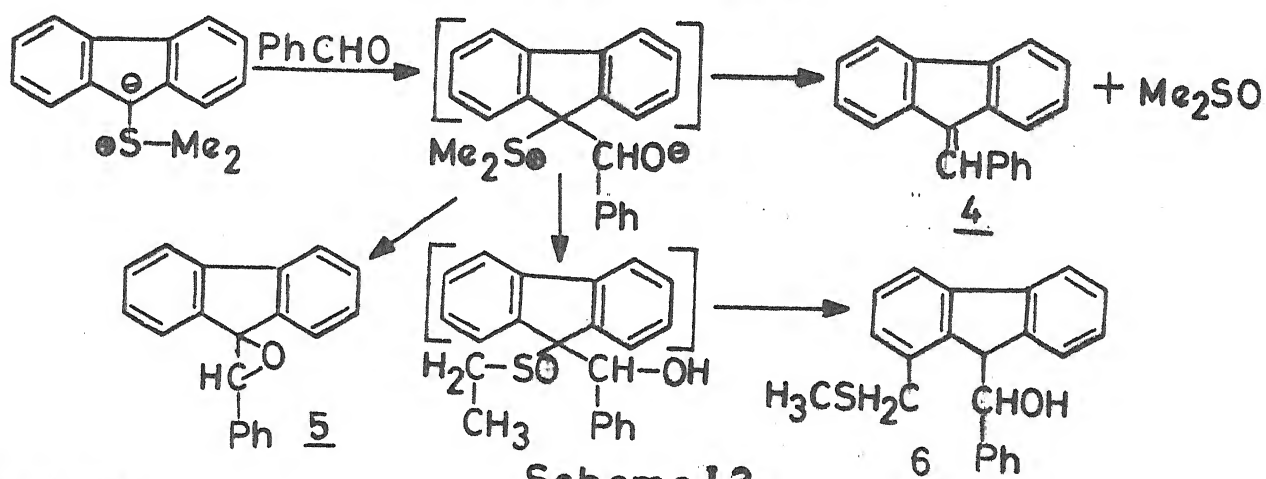
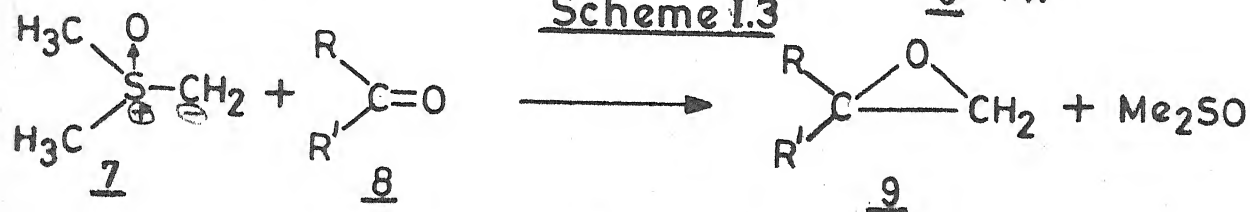
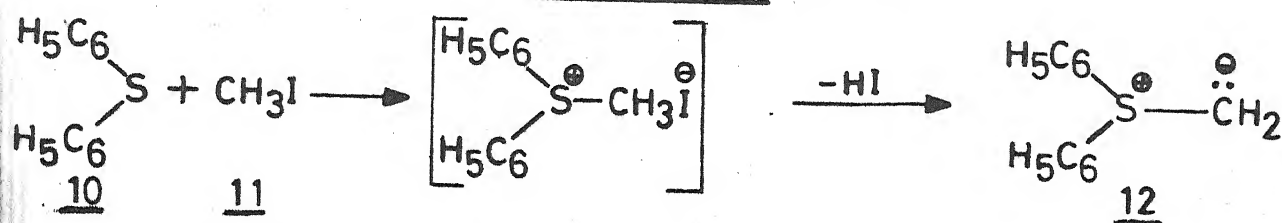
Ingold and Jessop's²⁶ earlier investigations gave the synthetic chemistry of S-ylides in 1930. His success was the isolation of a stabilized π -sulfuranes, a fluorenylidene

dimethyl sulfuranes (3) by reactivity 9-fluorenyl-dimethyl sulfonium bromide (2) with aqueous Na_2CO_3 (Scheme I.1). This class of compounds could not get the success regarding their reactivity and synthetic potentialities in the literature it showed an isolated event. But in the early sixties a flurry of activities when G. Wittig²⁷, isolated successfully and studies the reactivity of p-ylides towards carbonyl compounds. It was his concluding fact that any molecular system capable of providing adequate stabilization to a carbanion may form an ylide²⁸ system and prompted from Wittig investigation in the p-ylide chemistry. An active interest revived by Johnson and Lacount²⁹ when they isolated fluorenylidene dimethyl sulfurane (3) successfully. Reactivity of the some ylide (3) having the fact that the ylide afforded sufficient stabilization due to delocalisation of the lone pair of electron present on the ylide carbanion as shown by resonating structures (3 a,b,c) and therefore prevented the ylide (3) from being entered into reaction electrophillic substrate could not be studied too by them. With benzaldehyde the reaction of ylide (3), form 9-benzalfluorene was failed because it provided benzalfluorene oxide (5) and phenyl -9 (methythiomethyl) fluorenyl carbinols(6) in the place of benzal fluorene (Scheme I.2).

In connection the same Corey and Chaykovsky³⁰ reported reactions of the prepration more reactive and a less stable ylide methylenedimethyl oxosulfonium ylide (7). Having the

Schemes

(where X may be N, P, As, S etc.)

Scheme 1.1Scheme 1.2Scheme 1.3Scheme 1.4

ability of P-ylides to act as a good carbonyl olefinating reagent²⁷ Corey et al³¹ have also tried to react oxosulfonium ylide (7) with aldehydes and Ketones (8) and assumed to get the olefins but failed because the exclusive products were epoxides (9) (Scheme I.3).

In accordance with these observations oxosulfonium ylides were known as a versatile status of epoxidation reagents. Now an exclusive efforts were made to explore the synthetic potentialities of these ylides.

After this Franzen and Driessen³² made a successful attempt to synthesize a new kind of π -sulfuranes so called sulfonium ylides (12). Through the interaction of methyl phenyl sulfide (10) with methyl iodide (11) followed by Dehydrohalogenation (Scheme I.4). In comparison to oxosulfonium ylide (7), the ylide (12) so formed was less stable. This has been represented by the fact that the ylide gets decomposed in the absence of suitable substrates.

In the subsequent years Corey and Chaykovsky³³ have reported that sulfonium ylides undergo not only methylene transfer reaction on carbonyl group to form epoxides but also add on C=C, having some unsaturated groups in conjugation to form cyclopropanes. So methylene dimethyl sulfurane identified itself as appropriate epoxidation reagent to provide oxirane(13). Oxosulfonium methyllide has capabilities to add on to activated

C=C to form cyclopropanes (14). Thus undoubtedly π -sulfuranes are the best methylene transfer agents (Scheme I.5)³⁴. In coming years, the synthetic potentialities of π -sulfuranes have further been realized and illustrated in many ways with a view to test the domain of the applicability of these ylide systems as evidenced by recent monographs several comprehensive review articles³⁵⁻⁴¹.

A type of classes of π -sulfuranes are known the most common being sulfonium ylide (15), oxosulfonium ylide (16), sulfenyl ylides (17), sulfinyl ylides (18) and ~~imino~~ imino sulfuranes (19).

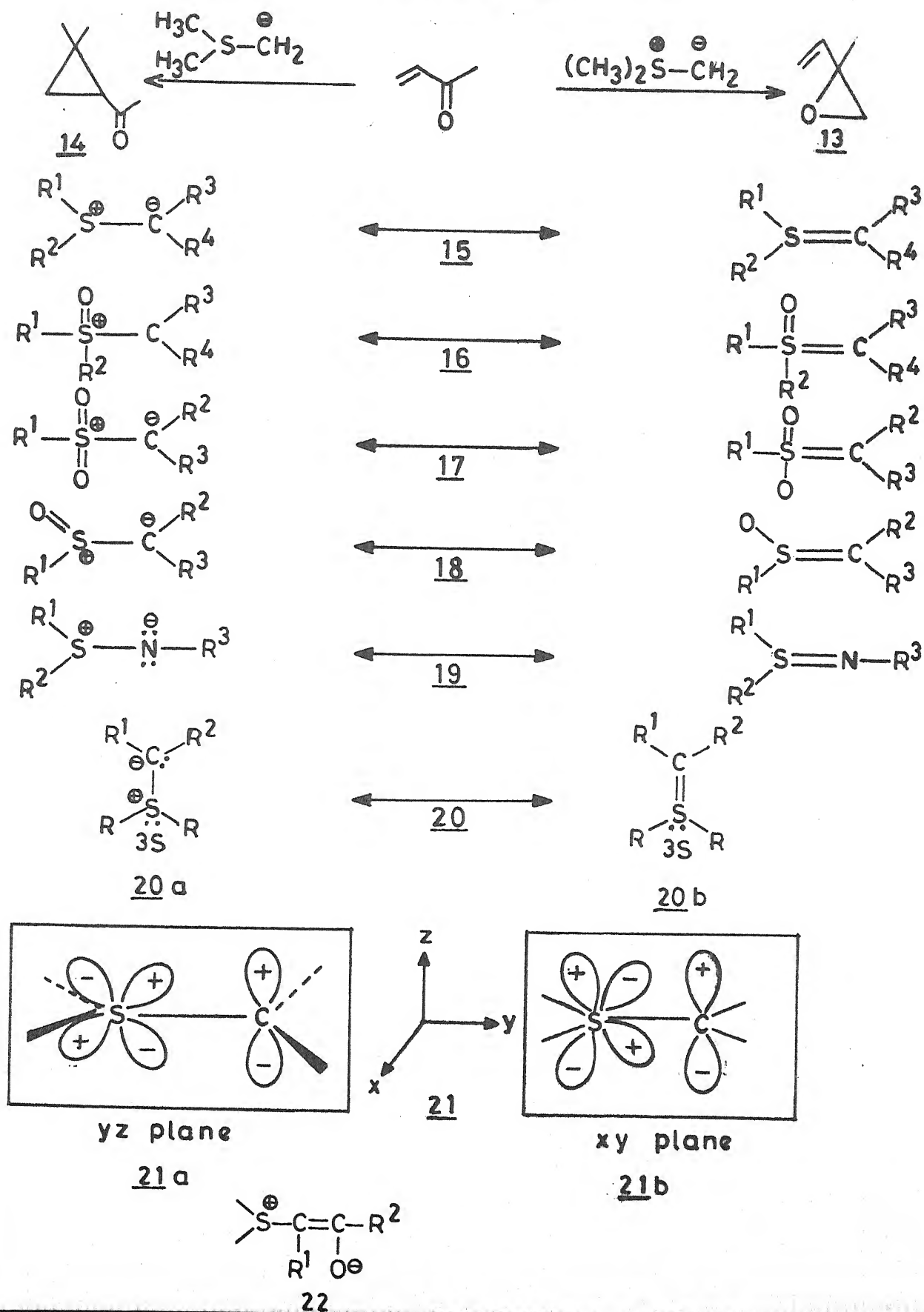
The stability of π -sulfuranes may be attributed to the electrostatic stabilization as well as delocalization of charge on the ylidic carbanion with d-orbitals of S-atom⁴²⁻⁴³. The magnitude of electrolytic stabilization of π -sulfuranes is completely controlled by the magnitude of charges present on the onium group as well as on the carbon ylide. Illustrating to this fact it can be observed that oxosulfonium ylides are more stable than their sulfonium counter parts, having to the increased positive charge on the S-atom due to the presence of more electronegative oxygen atom. The another factor which also makes a notable contribution to the stability of π -sulfuranes (20) is delocalization involving the use of 3d-orbitals which is the maximum. If the sulfur atom carries a full unit of (+ve)

charge. The overlapping of doubly occupied 2p-orbital of the ylide carbon with the formation of π -bond while the lone pair on S-remains in a 3p-orbital. This can be represented in the resonance hybrid of two limiting structures, the ylide form (20a) and the ylene form (20b). These factors are sufficient enough to explain as to why a series of π -sulfuranes have been isolated and characterized as stable species. Further more the maximum overlap of a 2p-carbon orbital (21a) with a 3d-orbital of S-atom is reported only when the molecule had the tendency to become coplanar (21b) & can be represented by $p_{\pi} - d_{\pi}$ orbital overlap structure (21).

However from recent ESCA data it has been concluded that the stability of these ylides is also influenced by the presence of certain electronegative groups on the ylide carbon. The reason is that the formal (-ve) charge on the ylide carbon actually, highly delocalization into substitution attached by the ylide carbon (22).

The reactivity of π -sulfuranes depends on the properties of the carbanion as well as the possible involvement of the heteroatom^{33,44-53}. Usually alkylidene sulfuranes of less stability show high reactivity whereas highly stabilized alkylidene sulfuranes show less reactivity. The reactivity of alkylidene sulfuranes is influenced by the distribution of the (-)ve charge over the molecule which, in turn, depends

Scheme 1.5



on the nature of the substituents R^1 and R^2 in the alkylidene position as well as on the group R on sulfur. Thus the nucleophilic character of the sulfurane decreases if the lone pair of electron on the α -carbon atom of the form (20a) is delocalized into group R^1 and R^2 tend to stabilize the (-)ve charge and consequently reduce the reactivity of the ylides.

On the otherhand, when there is no such interaction, an extremely reactive and unstable π -sulfurane is formed.

Prompted from the enhanced reactivity and easy preparation of the π -sulfuranes, it was to be thought of interest to focus our attention on synthesizing some new sulfonium ylides with a view to test their reactivity towards a variety of electrophilic substrates, resulting into the formation of diverse carbocyclic and heterocyclic systems⁵⁴⁻⁵⁷.

I.1. PREPARATION OF π -SULFURANES VIZ. SULFONIUM YLIDES :

I.1.1. π -Sulfuranes from sulfonium salt :

This remains the most common method of generating π -sulfuranes and involves the reactions of sulfonium salt with a base which is strong enough to abstract proton from α -carbon. In principle, any sulfonium salt (23) carrying at least one α -hydrogen is convertible into an ylide (24) (Scheme I.6). In practice the salt method is applicable only for three structural situations. In the first instance, all the

three of the groups attached to the S-atom must be identical so that it makes no difference which α -hydrogen removed by the base. In the second instance one or the two of the substituents have no α -hydrogen but these groups which do are identical³². The first and the last structural situation in which the sulfonium salt method²⁶⁻⁵⁴ is applicable necessitate there being an appreciable difference in the acidity of various available α -hydrogens and the availability of a base of the proper strength. The deprotonation of the more acidic α -hydrogen is always preferred. If the sulfonium salt (25) possesses three different kind of α -hydrogen and each of approximately the same acidity, then a mixture of π -sulfuranes results (Scheme I.7)

Numerous bases have been employed for the generation π -sulfuranes and the strength of base to be used depends on the acidity of the sulfonium salts. Thus trialkyl sulfonium salts required very strong bases such as methyl lithium⁵⁵, potassium-*t*-butoxide^{29,56} in dimethyl sulfoxide or methyl sulphinyl carbanion³²⁻³³. Further literature survey revealed that in the generation of stabilized π -sulfuranes only relatively weak bases such as trimethylamine, aq.NH₃ or aq.NaOH⁵⁷ are respectively required. Also solvents such as dimethyl sulfoxide or tetrahydrofuran are reported to be used for the non stabilized π -sulfuranes⁵⁸. Protic organic solvents or water have been shown to react with the non stabilized π -sulfuranes and therefore these solvents have not been employed

for their generation⁵⁹⁻⁶¹ of π -sulfuranes.

I.1.2. π -Sulfuranes from benzyne and organic sulfides :

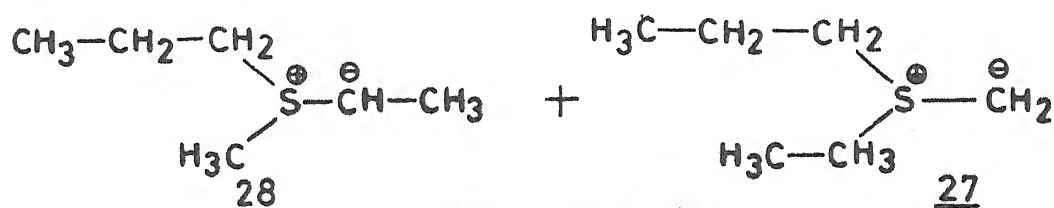
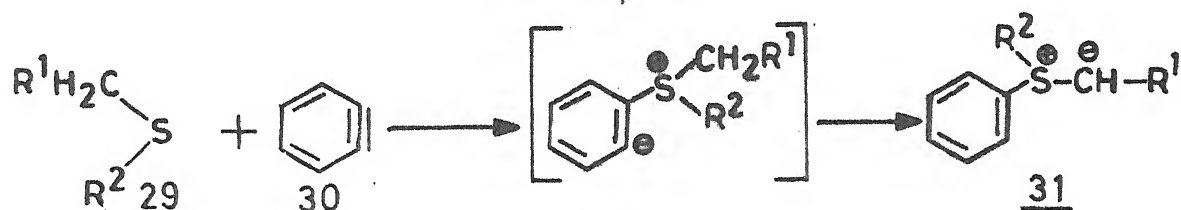
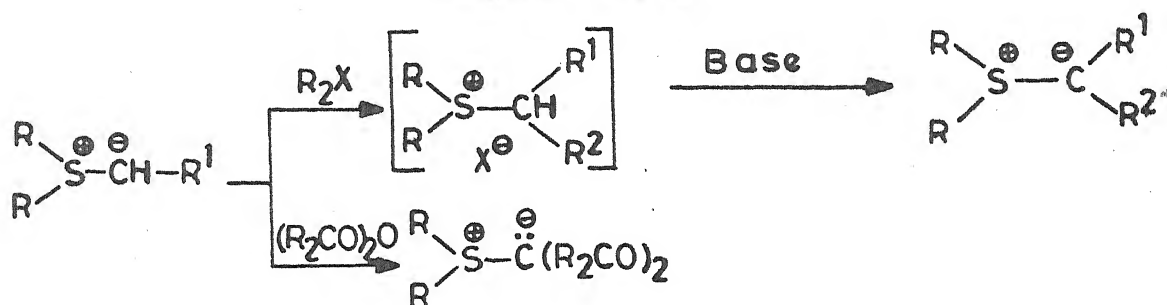
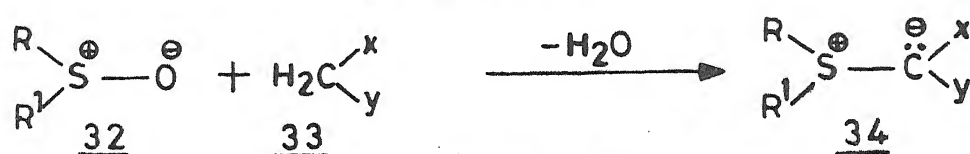
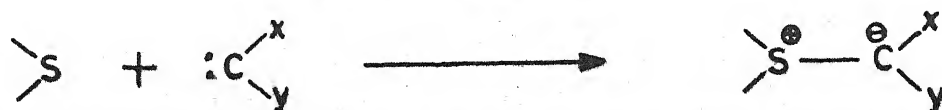
Among few other methods employed for the generation of π -sulfuranes are involving the reaction of dialkyl sulfides (29) with benzyne (30) is used for generation of such π -sulfuranes (ylides) (31). In which S-atom of the ylide carried one phenyl ring⁶⁶. But in practice, this method is of little importance. Because the presence of phenyl ring in resulting ylide renders them less reactive due to delocalization of the (+)ve charge carried by S-over phenyl ring (Scheme I.8).

I.1.3. π -Sulfuranes via alkylation and acylation method :

A wide variety of complex which are quite inaccessible by the conventional salt method have been prepared by the method called alkylation⁶⁷ or acylation⁶⁸. The method involves the interaction of the simple ylides with alkylating or acylating reagent to form more substituted stabilized ylides (Scheme I.9).

I.1.4. π -Sulfuranes from active methylene compound and sulfoxides :

The condensation of active methylene group (33) with sulfoxides or alkoxy sulfonium salts (32) offers a direct-route for the synthesis of highly stabilized ylide (34) via intermediate salt formation⁶⁹⁻⁷¹ (Scheme I.10).

Scheme 1.6Scheme 1.7Scheme 1.8Scheme 1.9Scheme 1.10Scheme 1.11

The reaction with sulfoxides is favoured in presence of dehydrating agents. In general acetic anhydride, phosphorous pent oxide, phenyl isocyanate and dicyclohexyl carbo di-imide-phosphoric acid are highly suitable for bringing about the desired results.

I.1.5. π -Sulfuranes from carbenes :

The addition of to a sulfide provides a most direct synthesis of π -sulfuranes (Scheme I.11)⁷²⁻⁷⁴ Diazo compounds serve as the good source of carbene intermediate for the preparation of ylides (37). The copper catalyzed thermal or photolytic decomposition of diazo compounds (36) in presence of an allyl or benzyl sulfide (35) appears to be the most attractive synthetic technique (Scheme I.12). However it was observed that thermal decomposition of diazo compounds is more suitable for synthesizing ylides.

I.1.6. π -Sulfuranes via Michael addition to vinyl sulfonium salt :

The Michael addition to a vinyl sulfonium salt (38) also produces π -sulfuranes⁷⁵⁻⁷⁶ (Scheme I.13). The resulting ylide (39), if stable is isolable and can be trapped by the attack of suitable reagents or it can further react intermolecularly.

I.1.7. π - Sulfurane from electrochemical reduction of sulfonium salts :

Only one example relating to the preparation of ylide (41) by this method is given in the literature⁷⁷, which involves the reduction of trimethyl sulfonium salt (40) in DMSO solution (Scheme I.14).

I.1.8. π - Sulfuranes from other methods :

Dimethyl sulfonium methylide is capable of being prepared in good yields by the phase transfer catalysis⁷⁸. A ligand exchange reaction between triphenyl sulfonium cation and cyclopropyl lithium gives diphenyl sulfonium cyclopropylide⁷⁹ in good yields. The synthesis of Thiaranes⁸⁰ and an asymmetric synthesis Thiaranes⁸¹ by the reaction of aldehydes and ketones with S-lithiomethyl-O-(-)-methyl dithiocarbonate have been reported recently.

I.2. REACTIONS OF π -SULFURANES :

I.2.1. Phenacyl dimethyl sulfonium bromide (with halogen acids) :

Ratt's et al⁵⁷ have reported that phenacylidene-dimethyl ylide on its reaction with HBr acid affords dimethyl phenacyl sulfonium bromide. Jhonson et al⁶⁸ tested the reaction and demonstrated that almost all the carbonyl stabilized sulfonium⁴² ylides react with hydrogen bromide (43) to form

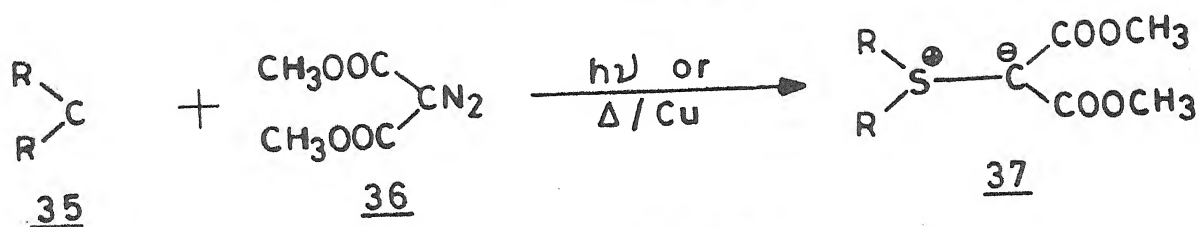
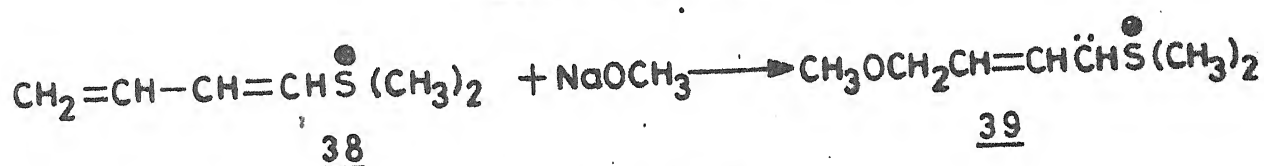
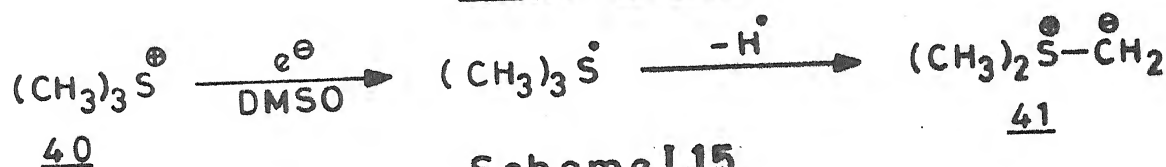
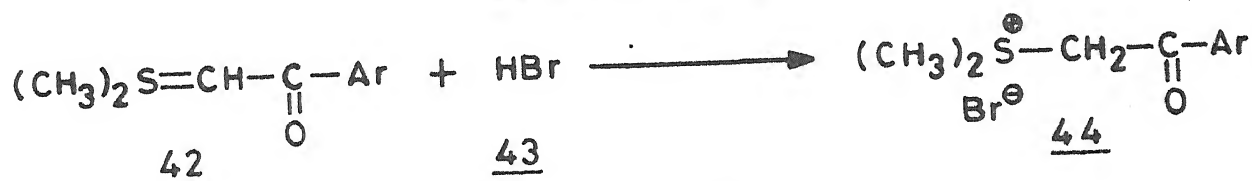
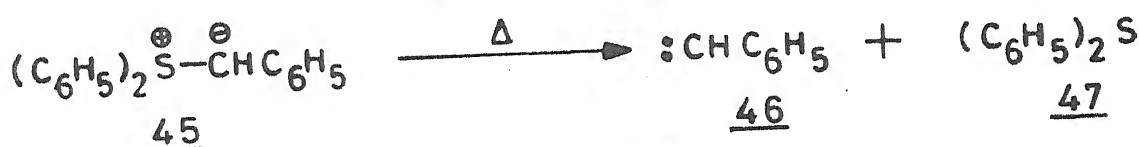
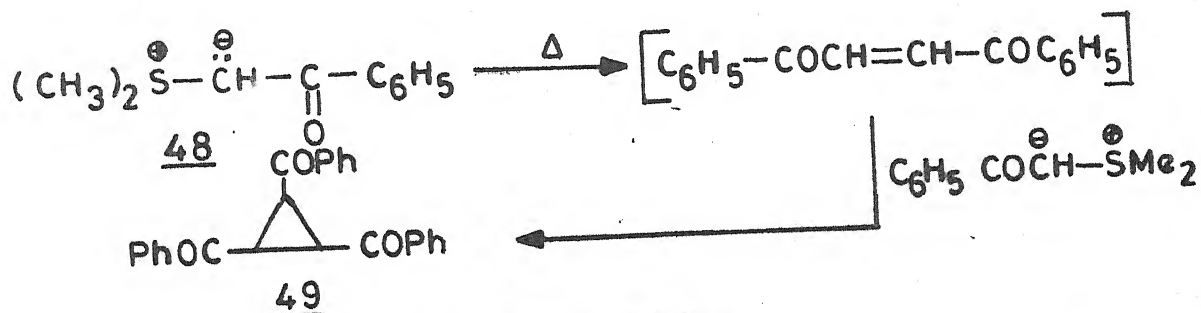
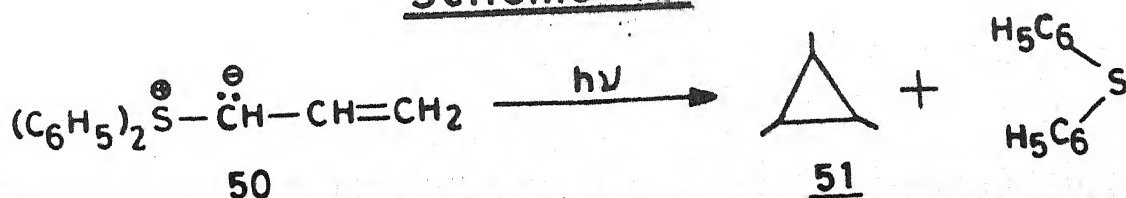
conjugate acid (44) of the ylide (42) (Scheme I.15). These observations clearly indicate that sulfonium ylides are nothing but the conjugate bases of dimethylphenacyl sulfonium bromide.

I.2.2. Thermolysis of π -sulfuranes :

The existing literature lacks in sufficient information concerning the thermolysis of sulfonium ylides. However Jhonson et al⁷⁰ have shown that the non stabilized sulfonium ylide, diphenyl sulfonium benzylide (45), on thermolysis dissociates into carbenes (46) and phenylsulfide (47) (Scheme I.16). On the otherhand, thermolysis of stabilized ylide, phenacylidene dimethyl sulfurane (48), takes different course⁸²⁻⁸³ where carbene generated by the thermal dissociation of the ylide dimerises to form dibenzoylethylene which, in turn, is attacked by one mole of the original ylide (48) affording 1,2,3-Tribenzoyl-cyclopropane (49) through carbenoid mechanism (Scheme I.17).

I.2.3. Photolysis of π -sulfuranes :

Photolytic conversion of the π -sulfuranes has been less studied. However Trost et al⁸⁴ have reported that photochemical decomposition of diphenyl sulfonium allylide (50) occurs in which cyclopropane (51) is isolated in 25% yields (Scheme I.18). Subsequent to this Corey and Chaykovsky⁸⁵ developed an Arndt- Eistert type of process to yield esters (54) by irradiation of β -keto-oxosulfonium ylide (53) prepared

Scheme 1.12Scheme 1.13Scheme 1.14Scheme 1.15Scheme 1.16Scheme 1.17Scheme 1.18

by acylation of methyllide (52) (Scheme I.19).

I.2.4. Tribenzoyl cyclopropane(with α -bromo ketones):

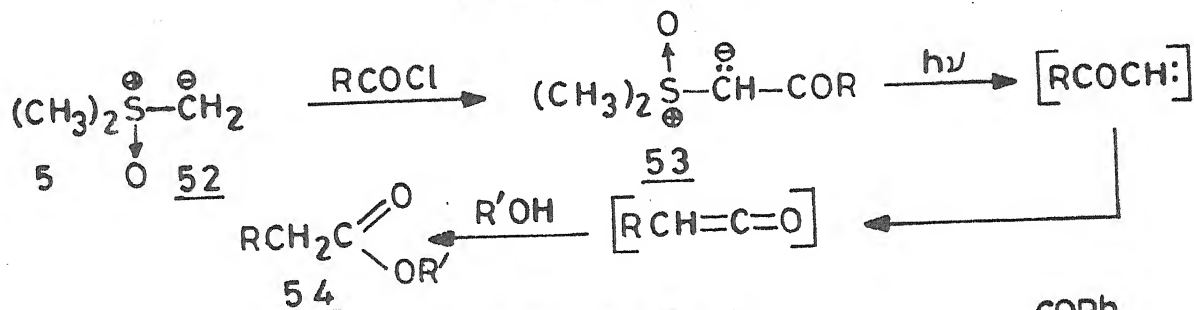
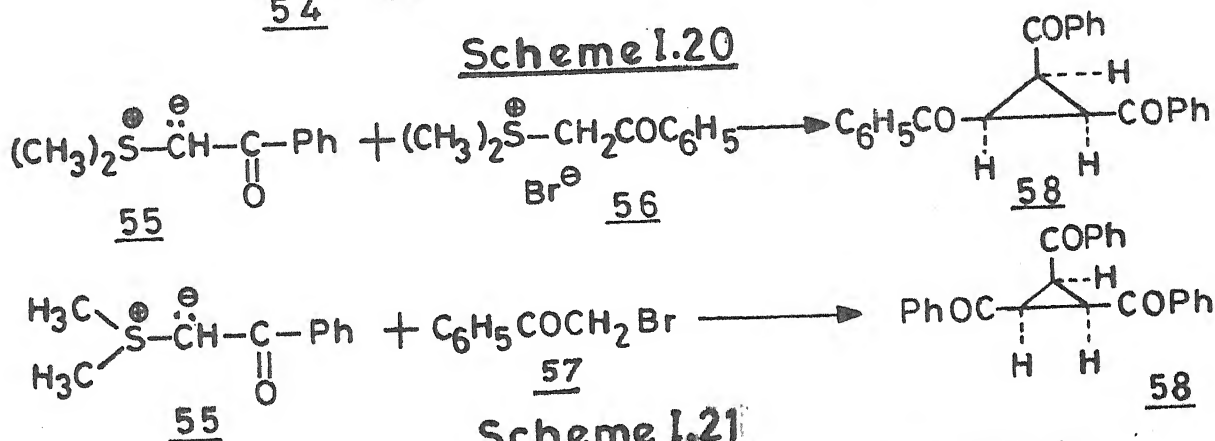
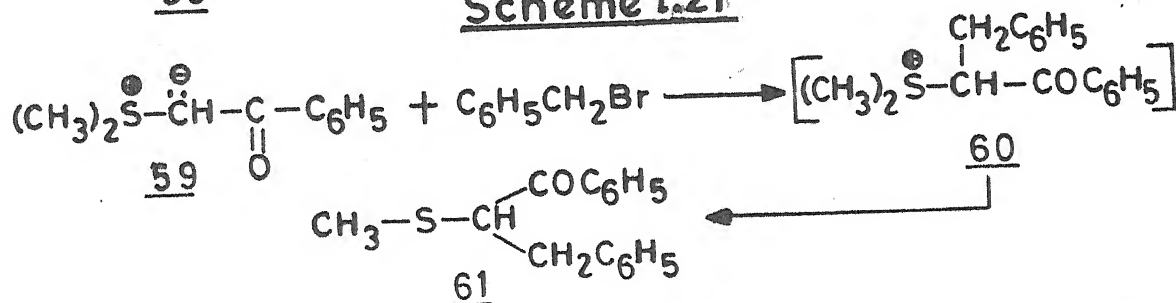
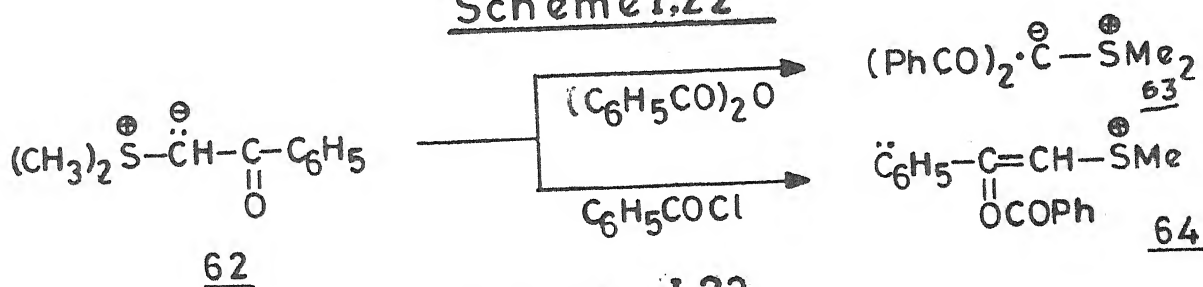
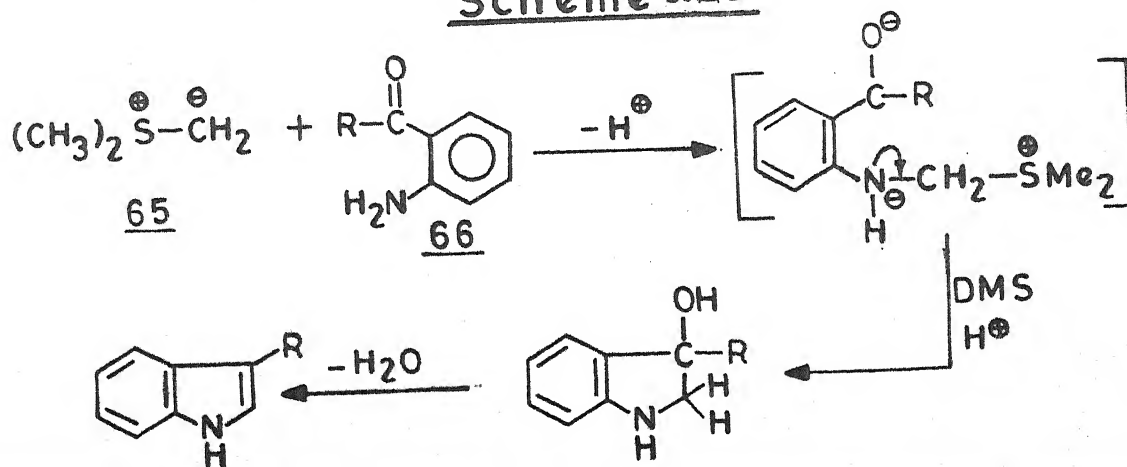
Jhonson et al⁸⁶ have reported that the phenacylidine dimethyl sulfurane (55) reacts either with its conjugated acid (56) or phenacyl bromide (57) to afford tribenzoyl cyclopropane (58). The mechanism of the reaction appears to involve an acylation elimination addition sequence(Scheme I.20).

I.2.5. Alkylation of π -sulfuranes :

The alkylation reactions have assumed importance because of their ability to offer a versatile route for synthesis of disubstituted ylides which are otherwise difficult to prepare. Other route Jhonson et al⁶⁸ studied the alkylation of phenacylidine dimethyl sulfurane (59) with benzyl bromide(60) where α -methyl-thio- β -phenyl propiophenone (61) was reported to have been formed (Scheme I.21).

I.2.6. Acylation of π -sulfuranes :

Based on information gathered so far non stabilized π -sulfuranes are not liable to be attacked by acylating reagents. However stabilized π -sulfuranes are reported to undergo acylation reaction with a couple of acylating reagents⁶⁸⁻⁸ and it is observed that the course of acylation depends on the nature of the acylating reagents. Thus phenacylidenedimethyl-sulfurane (62) on reaction with benzoic anhydride undergoes

Scheme I.19Scheme I.20Scheme I.21Scheme I.22Scheme I.23

C-alkylation to afford a new ylide (63). On the otherhand ylide (62) follows O-acylation when treated with benzoyl chloride, thus affording enol benzoate(64) (Scheme I.22).

I.2.7. Synthesis of Indoles : (Reaction with amino compounds)

Bravo and his coworkers⁸⁸ have synthesised a wide variety of substituted indoles (67) by the reaction of dimethyl sulfonium methylide (65) with aromatic-o-amino carbonyl compounds (66) (Scheme I.23). Later on Junjappa³⁵ reported the formation of 2-substituted indoles (70) by the interaction of carbonyl stabilized sulfuranepheneacylidene dimethyl sulfurane (68) and substituted anilines (69) in the presence of diethylaniline (Scheme I.24).

I.2.8. Benzothiophenes (Reaction with mercapto compound) :

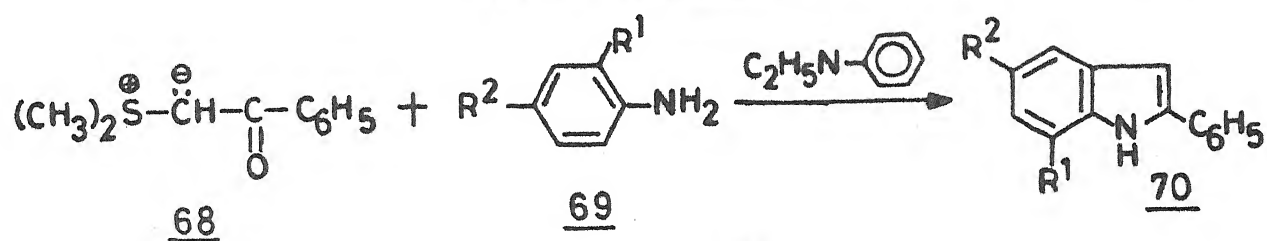
Bravo et al⁸⁹ have demonstrated that dimethyl sulfonium methylide (72) is capable of undergoing reactions with o-mercapto ketones (71) forming benzothiophenes (73) (Scheme I.25).

I.2.9. Pyrazole derivatives (Reaction with nitrile amine) :

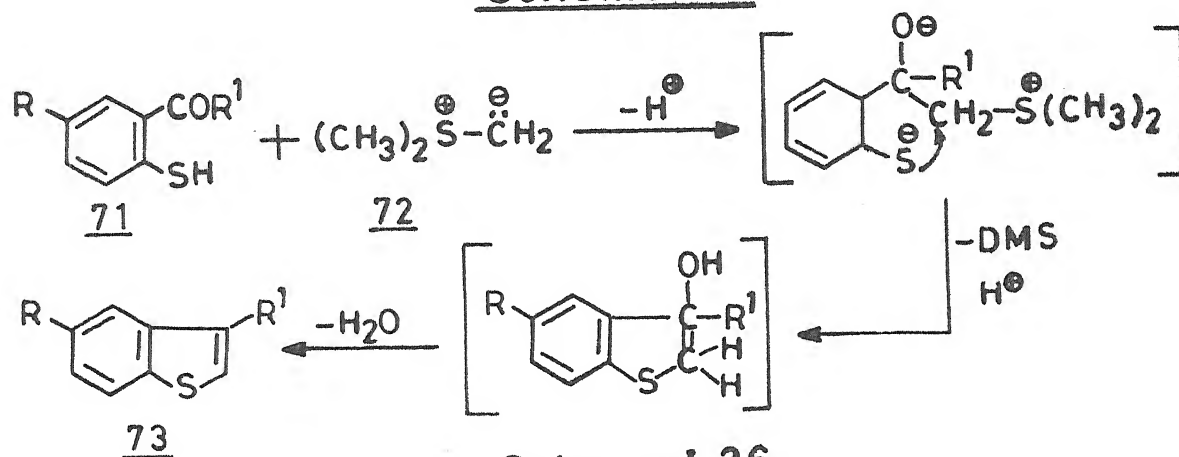
The carbonyl stabilized sulfonium ylides have also been reported in literature⁹⁰ to undergo reaction with nitrimines affording pyrazole derivatives. For example, the reaction of stabilized sulfuranes (74) with N-(α -chlorobenzylidene)

Scheme I.24

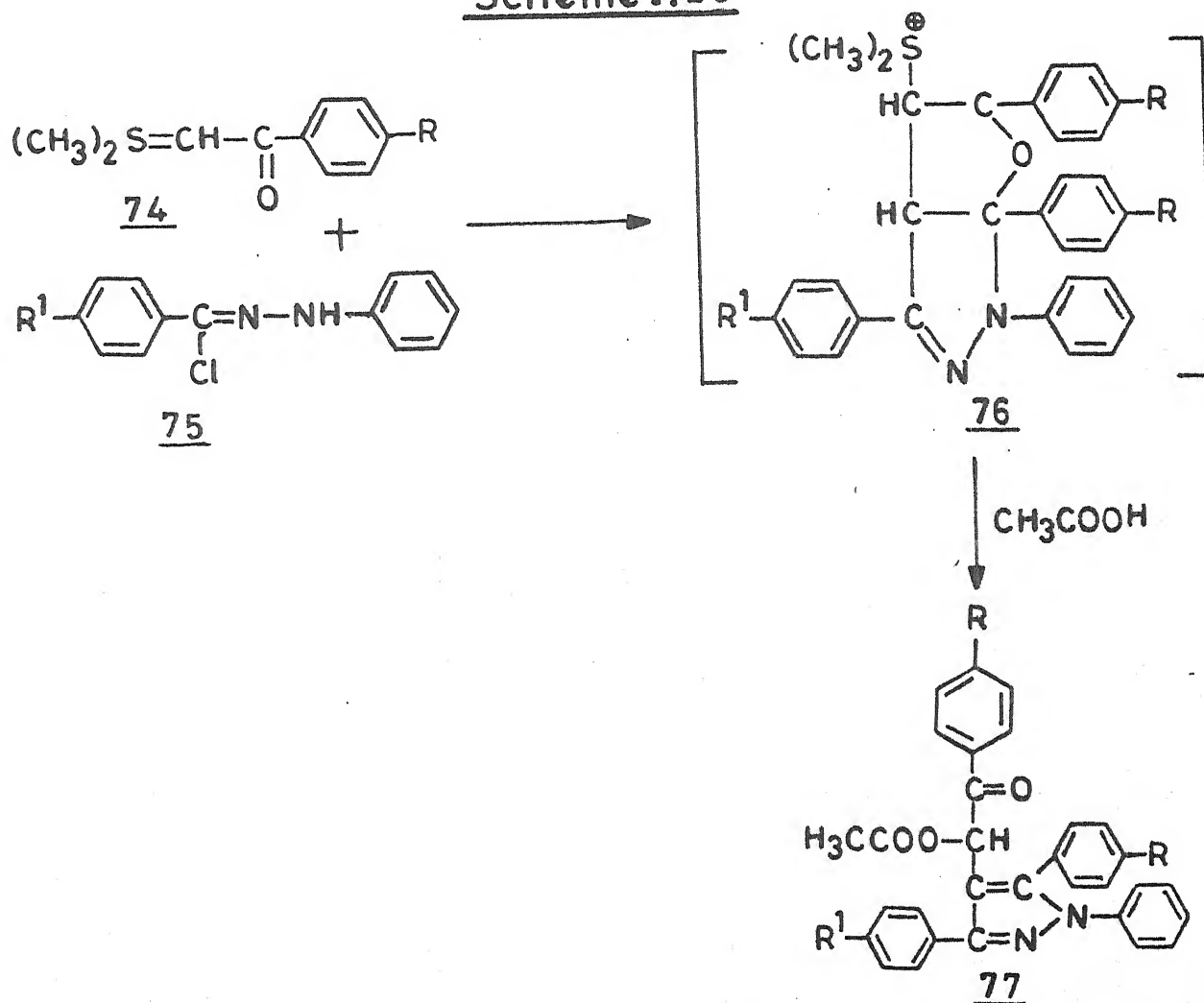
21



Scheme I.25



Scheme I.26



N-phenyl hydrazine (75) affords pyrazole (77) via intermediacy of the cyclic products (76). This reaction has assumed big importance in the synthesis of pyrazole derivatives (Scheme I.26).

I.2.10. With multiple bonds :

2.10.1. With C=O double bonds :

The best known reaction of sulfonium ylides which attained importance in the preparative organic chemistry under the name of epoxidation involves the combination of these ylides (78) with carbonyl compounds (79) to form oxiranes (81) exclusively. The reaction proceeds via the intermediacy of betaine type of compound (80) formed by the nucleophilic attack of the ylidic carbonium on the carbonyl carbon atom and involving displacement by the oxyanion on the carbon carrying the onium group. It appears⁹¹ in the case of sulfonium betaine (80) that the potential S-O bond formation is not a sufficient driving force to dictate the course of the reaction (Scheme I.27). The conjugation and stabilization afforded by the substituents (R^1) present on the ylide as well as on the carbonyl group (R^2, R^3) to an incipient double bond in the transition state appears to be the rate controlling factor.

In the absence of such stabilisation oxiranes formation may very easily by the normal course of events as is observed in the case of methylides⁹².

Non stabilized π -sulfuranes eg. methylenedimethyl-sulfurane (82) when reacted with carbonyl compounds (83) such as benzaldehyde cyclohexanone and benzophenones afforded the epoxides (84) in fair to good yields (Scheme I.28). In the year 1961, Franzen et al⁵⁶ further extended the reaction of these ylides with α, β -unsaturated ketones and have shown that the exclusive formation of epoxides and non isolability of cyclopropanes. In the subsequent years Jhonson et al^{60,93} took the credit of synthesizing substituted benzyldine phenyl sulfuranes (85) and have studied their reaction with carbonyl compounds (80) which lead to the formation of epoxides (87) exclusively (Scheme I.29). These study revealed that in π -sulfuranes unlike arsonium ylides⁹⁴, the course of the reaction with carbonyl compounds can not be attended by the nature of group present on the benzylic position of the ylide carbanion, as a result these ylides⁹⁵ have been successfully employed for the synthesis of nitro substituted stibenes oxides which are quite inaccessible by their arsonium counterparts owing to the fact that nitro group favours the reaction to proceed in the direction of olefins formation.

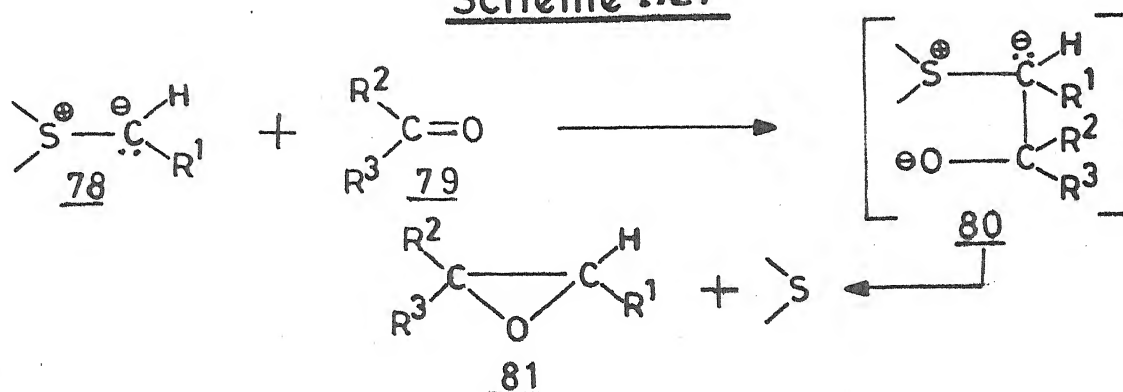
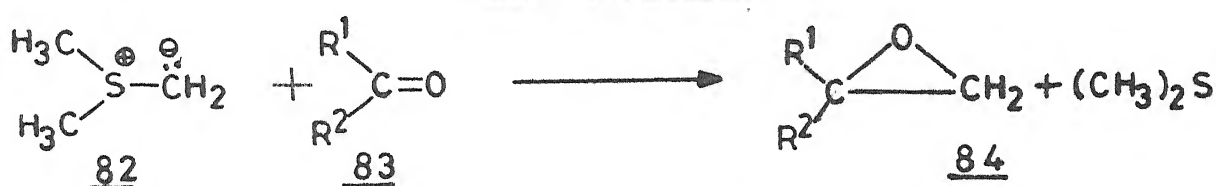
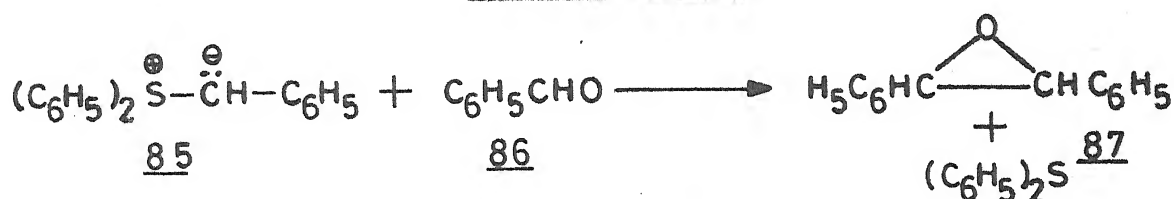
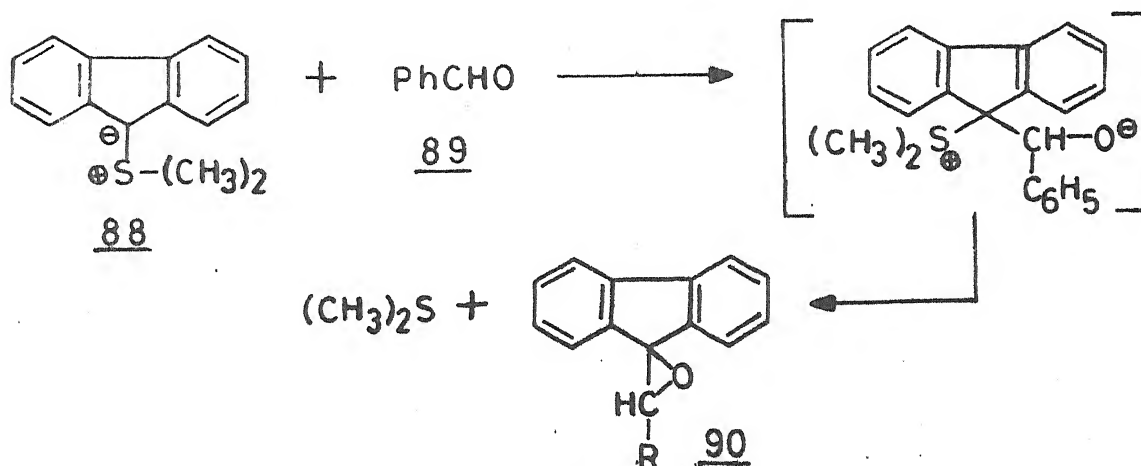
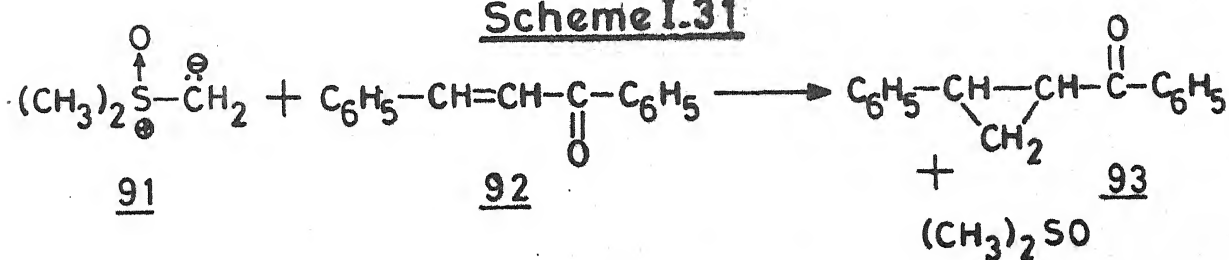
Unlike non stabilized π -sulfuranes which are quite reactive against carbonyl function giving epoxides exclusively. Stabilized sulfuranes⁶² do not react with carbonyl functions. Non reactivity towards carbonyl function is due to the decrease in nucleophilicity of these ylides. However Jhonson and Lacount²⁹

were first to study the reaction between stabilized π -sulfuranes fluorenylidene dimethyl sulfurane (88) and benzaldehyde (89), when epoxides (90) was found to be the exclusive product (Scheme I.30). Thereafter Payme et al⁹⁶ have demonstrated that stabilized ylides could be made to react with such systems in which carbonyl group is in conjugation with the highly electropositive group which enhances the electrophillic charecters of carbonyl atom, thus making them to enter into reaction with the sulfonium ylides.

2.10.2. With C=C double bonds(Synthesis of cyclopropane):

Prompted by the ability of π -sulfuranes to act as a versatile methylene transfer reagent as evidenced by the fact they form epoxides on their attack on carbonyl function, curiously aroused among the organic chemists to explore the reactivity of sulfuranes towards C=C. One of the first attempts in this direction came in the form of investigation carried out by Corey and Chaykovsky³⁰⁻³³ which involved the nucleophillic addition of dimethyl oxosulfonium methyllide (91) with chalcone (92) to produce trans-1-benzoyl-2-phenyl cyclopropane (93) (Scheme I.31).

However cyclopropanation reactions starting from sulfonium salts (94) to form 1,2,3-tribenzoyl cyclopropane(97) were also known earlier⁹⁷ although the reaction mechanism of the reaction was not clear. Only in 1966 it was demonstrated⁸²⁻⁸³

Scheme 1.27Scheme 1.28Scheme 1.29Scheme 1.30Scheme 1.31

that the reaction proceeded by the addition of dimethylsulfonium phenacylidene (95) to dibenzoyl ethylene (96) (Scheme I.32). However the case with which cyclopropanation takes place depends on the nucleophilic character of the ylide carbanion. This can be illustrated by the fact that non-stabilized π -sulfuranes readily attack over C=C bond, due to enhanced nucleophilicity by the absence of stabilization factors giving cyclopropane derivatives. On the otherhand, it was observed that stabilized sulfuranes which are relatively less nucleophilic attack on conjugated C=C system only.

Subsequent to these investigations the method introducing cyclopropanes has become one of the most ^{important} in daily methods besides one involving carbene addition. Payme⁹⁸ has shown by studying the addition of carbethoxy dimethyl π -sulfuranes (98) to the hexanone (99) that the nucleophilic methylene transfer takes place at the double bond to form cyclopropane (100) and not on carbonyl group (Scheme I.33). In this way cyclopropanated steroids⁹⁹ and nucleosides¹⁰⁰⁻¹⁰¹ have been synthesised.

2.10.3. With C-N double bond (Synthesis of Aziridines):

Franzen³² and Corey³³ have studied the reaction of non stabilized π -sulfuranes methylene dimethyl sulfurane (101), with Schiff's bases (102), leading to the formation of a variety of aziridines (103) (Scheme I.34). Hoffman¹⁰² et al have

demonstrated that the same ylide (101) can also affect other C-N double bond systems when he synthesised 1-azabicyclobutanes (105) by the direct condensation of the ylide (101) with aziridines (104) (Scheme I.35).

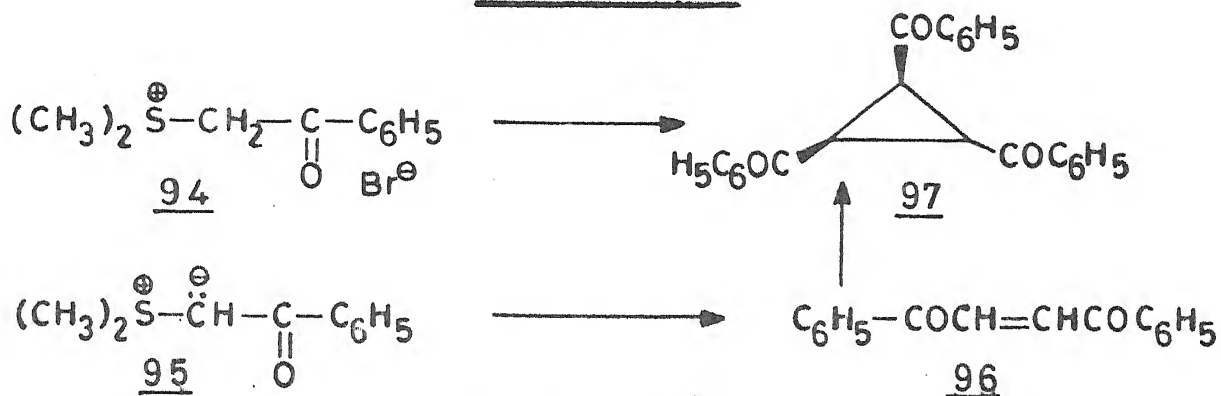
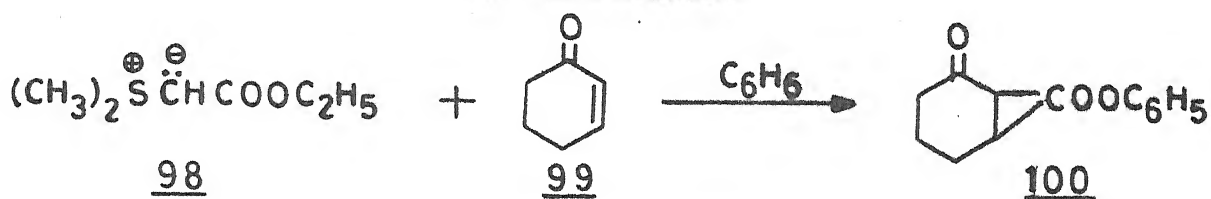
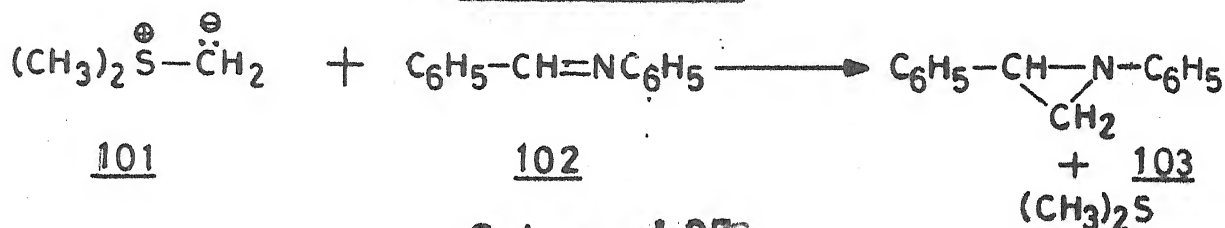
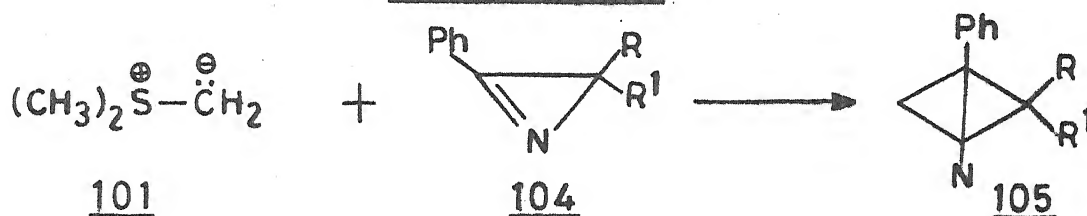
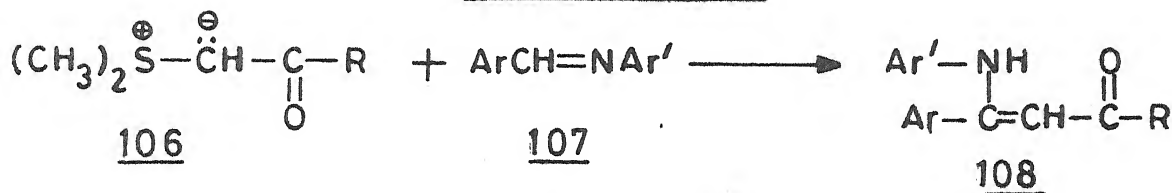
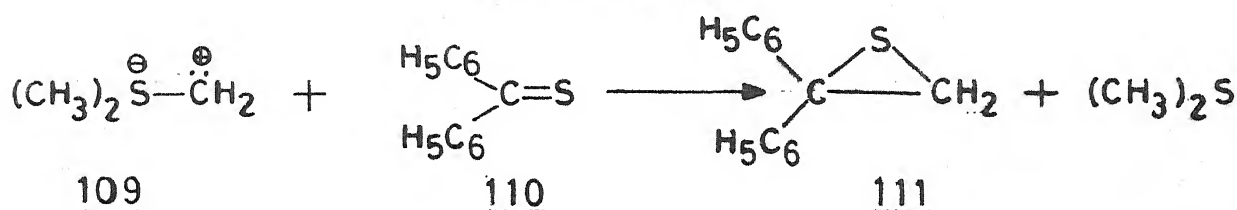
However the stabilized sulfonium ylides differ from the non stabilized sulfonium ylides in so far as their course of reaction with Schiff's bases is concerned and it was observed¹⁰³ that ylides (106) produce aryl amino cinnamates (108) and not aziridines (Scheme I.36).

2.10.4. With C-S double bonds (Synthesis of Thioxirane):

Corey and Chaykovsky³³ have reported that methylene dimethyl sulfurane (109) on its reaction with benzothiophenone (110) affects the methylene transfer at C=S bond affording the thiooxirane (111). The reaction follows the same course as with benzophenone (Scheme I.37).

2.10.5. With N-O double bond :

The reaction of nitro compound with sulfonium ylides leads to the synthesis of C-N double bond. Jhonson⁵⁴ demonstrated that it was fairly on addition, elimination methylene transfer reaction of sulfuranes which produces oxime. Thus fluoranylidene, dimethyl sulfurane (112) and nitrosobenzene (113) were shown to undergo an exothermic and rapid reaction to afford the nitro-N-phenyl fluorenone ketoxime (114) (Scheme I.38).

Scheme I.32Scheme I.33Scheme I.34Scheme I.35Scheme I.36Scheme I.37

I.2.11. Metalation of π -sulfuranes :

The metalation reaction of π sulfuranes could not be explored until recently only preliminary studies on the reactions of inorganic compounds with the yields are reported³⁶.

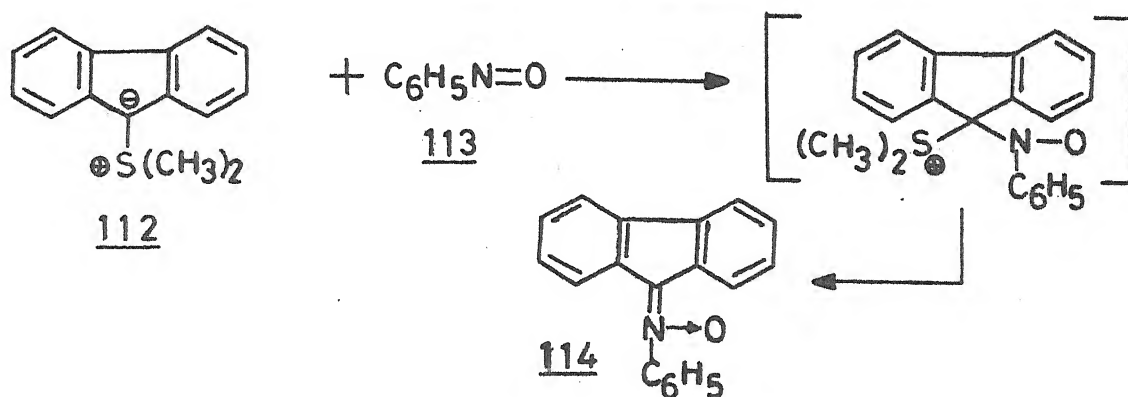
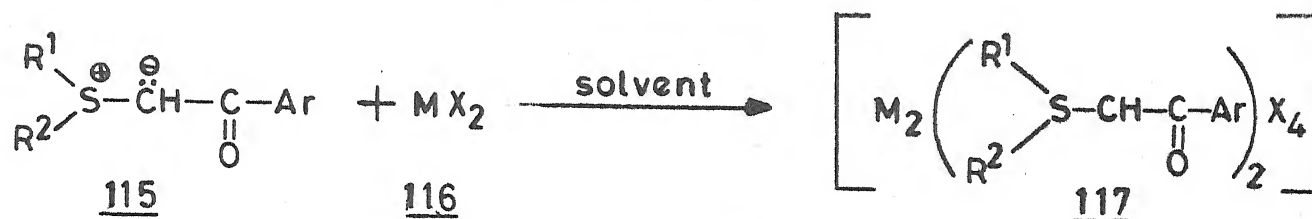
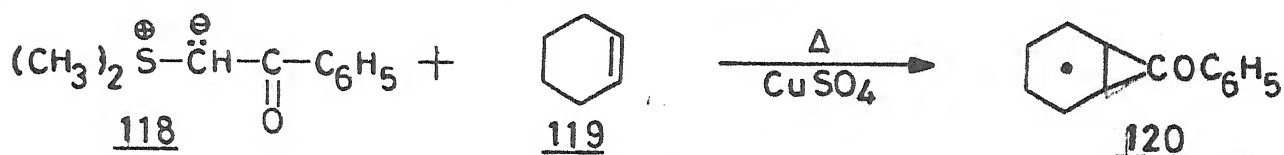
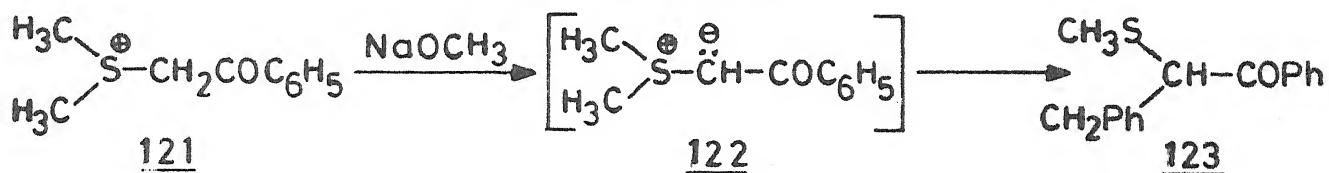
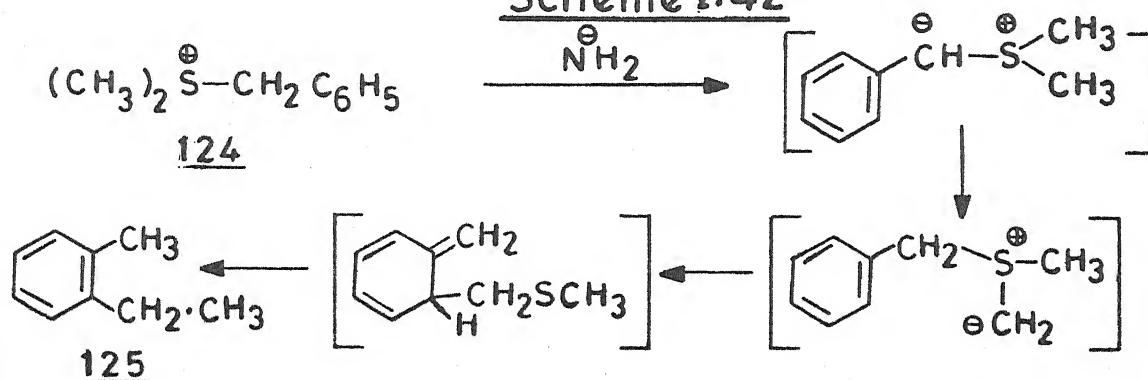
However it has been shown that the sulfonium ylides (115) being co-ordinatively unsaturated, 1,2 dipolar complex of carbon serve as a good ligand for transitional metals(116) in various oxidation states and yields the markedly stable metal complexes (117) of sulfonium ylides(115) (Scheme I.39).

I.2.12. Elimination :

Evidence for the α -elimination is meagre¹⁰⁴. However dimethyl sulfonium phenacylide (118) has been reported to add an cyclohexene (119) in the presence of cupric sulphate through α -elimination, giving cyclopropane (120)¹⁰⁵ other claims of α -elimination remain even more speculative.

I.2.13. Rearrangement :

As revealed by the literature π -sulfuranes have been involved in several types of rearrangements. Thomson and Stevans¹⁰⁶ have reported that benzylmethylphenacyl sulfonium bromide (121) undergo of phenacylidene benzyl methyl sulfurane (122) to yields the rearrangement product (123) (Scheme I.41). Houser et al¹⁰⁷ have demonstrated that the benzyl dimethyl

Scheme I.38Scheme I.39Scheme I.40Scheme I.41Scheme I.42

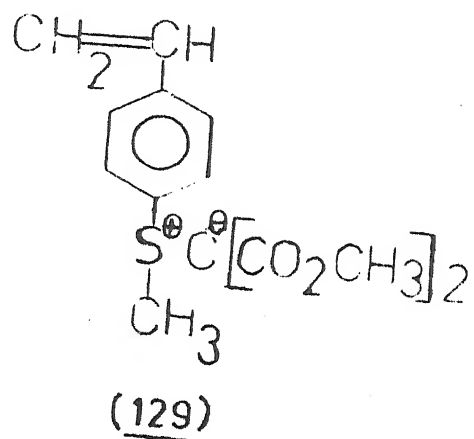
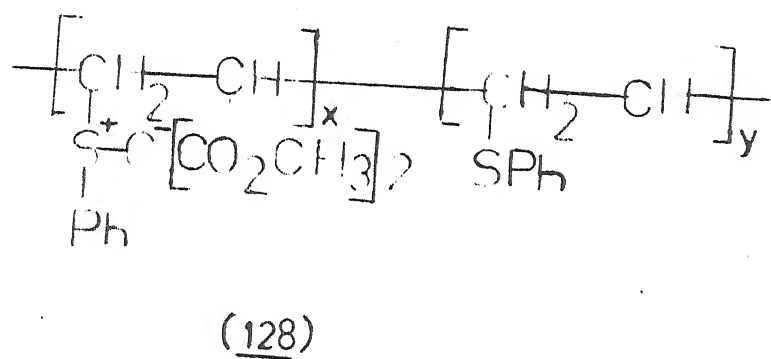
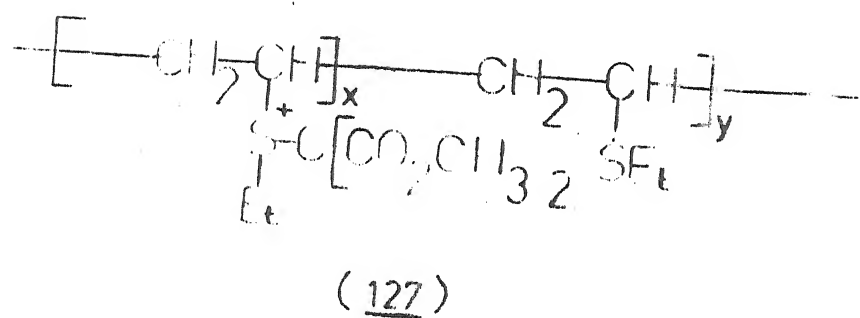
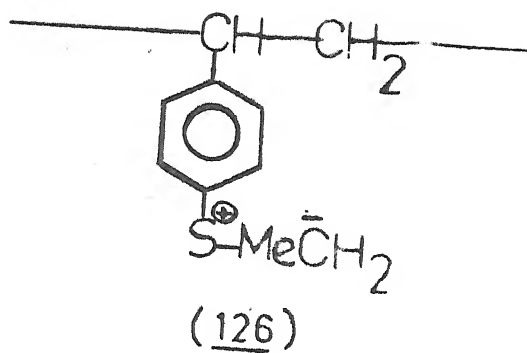
sulfonium ion (124) in the presence of amide ion, undergoes Sommetal rearrangement to afford O-methyl benzyl methyl sulfide (125) (Scheme I.42).

In recent years, these rearrangements have been produced to be great synthetic importance particularly in the synthesis of natural products^{72,108}.

I.2.14. π -Sulfuranes in the preparation of polymers :

In an attempt to prepare sulfonium ylide polymer viz. sulfurane polymer Tanimoto and et al^{109,110} coming out the reaction of sulfonium salt with benzaldehyde in presence of base and obtained styrene oxide. The reaction was carried out to proceed via ylide polymer formation (126) which was unstable and has not been isolated.

Later on Kondo et al¹¹¹ and his colleagues reported on the synthesis of poly (vinyl sulfonium ylide) with a trivalent sulfur attached directly to the polymer chain, Poly [ethyl vinyl sulfonium bis (methoxy carbonyl) methylide] (127) was prepared by irradiation of a benzene solution of poly (ethyl vinyl sulfide) and dimethyl diazomelionate in a pyrex tube by a high pressure mercury lamp. In the similar manner, an attempt was made to prepare poly [Phenyl vinyl sulfonium bis(methoxy carbonyl) methylide] (128), but it was not successful. However, this compound was obtained by the thermal reaction of



diazomalonate and poly (phenyl vinyl sulfide) in the presence of cupric sulphate as catalyst in benzene.

The structure of these ylide polymers were determined and confirmed by IR and NMR spectra. These were the first stable sulfonium ylide polymers reported in the literature. They are very important for such industrial uses as ion exchange resins, polymer supports, peptide synthesis, polymeric reagents and polyelectrolytes. Also in 1977, Hass Mereau¹¹² found that when poly (4-vinyl pyridine) was quaternized with bromomalonamide, two polymeric quaternary salts resulted. These polyelectrolyte products were subjected to thermal decyanation at 7200°C to give isocyanic acid or its isomer cyanic acid. The addition of base to the solution of electrolyte in water gave a yellow polymeric ylide.

In a pioneering article, Farrall et al¹¹³ reported the preparation of fully regenerable sulfonium salts anchored to an insoluble polymer and their ylides with carbonyl compounds. Their results clearly indicate that phase transfer catalysis is the method of choice for the generation of sulfonium ylides on insoluble resins from a polymeric sulfonium salt.

Kondo maintained his interest in this area and with his collaborators¹¹¹ he made detained investigation on the polymerisation and prepration of methyl-4-vinyl phenyl-sulfonium bis(methoxy carbonyl) methyllide (129) as a new kind of stable

vinyl monomer containing the sulfonium ylide structure. It was prepared by heating a solution of 4-methyl thiostyrene, dimethyldiazomalonate, and t-butyl catechol in chlorobenzene at 90°C for 10 hours in the presence of anhydride cupric sulphate and (129) was polymerized by using α - α' -azobisisobutyronitrile (AIBN) as initiator and dimethylsulfoxide as solvent at 60°C. The structure of polymer was confirmed by IR and NMR spectra and elemental analysis. In addition, this monomeric ylide was copolymerised with vinyl monomers such as methyl methacrylate (MMA) and styrene.

REFERENCES

1. G. Wittig and G. Felletschin Justus Liebigs Ann., Chem. 555, 133 (1944).
2. A.W. Jhonson, "Ylide Chemistry", Academic Press, New York (1966).
3. R. Hoffmann, D.B. Boyd and S.Z. Goldberg, J. Amer. Chem. Soc. 92, 3929 (1970).
4. J. Absar and J.R. Van Wazer, J. Amer. Chem. Soc., 93, 1063 (1971).
5. D.B. Boyd and R. Hoffmann, J. Amer. Chem. Soc., 93, 1063 (1971).
6. H.J. Bestmann and R. Zimmermann, "Organic Phosphorous Compounds", (G.M. Kosolapoff and L. Maier Eds), John Willy and Interscience, New York, 3, (1972).
7. H.J. Bestmann, "Newer method of preprative Organic Chemistry", (W. Foerst Ed.) Academic Press, New York, 5, (1968).
8. B.M. Trost and L.S. Melvin, Jr. "Sulfur Ylide", Academic Press, New York (1975).
9. A. Maercker "Organic Reactions", (R. Adam. Ed.) John Willey and Sons, New York, 14, 270 (1965).
10. I. Zugravescu and M. Petrovanu, "N. Ylide Chemistry", Editura Academiei Republicei Socialiste, Romania (1976).

11. U. Scholkopf, "Newer Methods of preparative Organic Chemistry". (W. Foerst, Ed.) Academic Press, New York, 3, 111 (1985).
12. P.A. Lowe, Chem.Ind.(London), 1070 (1970).
13. R.F. Hudson, Chem.Brit., 7, 287 (1970).
14. D.J.H. Smith, Organophosphorous Chem., 7, 1 (1976).
15. H.J. Bestmann, Angew Chem., 89, 361 (1977).
16. F. Krohnke, Synthesis, 1, (1976).
17. G. Surpateanu, J.P. Cattean and P. Karafiloglon, Tetrahedron, 32, 2647 (1976).
18. R.S. Tewari, A.K. Awasthi, Synthesis (4) 330, 334(1983).
19. R.S. Tewari, A.K. Dubey & N.K. Mishra, J.Chem.Eng.Data, 27, 101 (1982).
20. K.C. Gupta, R.K. Nigam and N. Srivastava, Current Sci., 53, 191 (1984).
- 20.a. K.C. Gupta, P.K. Pathak and B.K. Saxena, Indian Journal of Chemistry, 24B, 783 (1985); 25B, 196, 312(1986).
21. H. Pommer, Angew Chem.Int.Ed., 16, 432 (1977).
22. V.A. Nikolaev and I.K. Korobityna, Zh.Vser.Khim., 24(5).
23. S.K. Nigam and A.K. Srivastava, Acta polym., 38, 244 (1987).

24. S.K. Nigam, S. Saini and A.K. Srivastava, Accepted as a short Lecture in the 31st IUPAC Symposium.
25. R. Vashistha and A.K. Srivastava, *Acta polym.*, 40(5), 358 (1989).
26. C.K. Ingold and J.A. Jessop, *J.Chem.Soc.*, 713 (1930).
27. G. Wittig and U. Schollkopp and H. Pommer, *Chem.Abstract* 35, 4576 (1961).
28. A.W. Jhonson and R.B. Lacount, *Chem. & Ind.(London)*, 1440 (1958).
29. A.W. Jhonson and R.B. Lacount, *J.Am.Chem.Soc.*, 83, 417 (1961).
30. E.J. Corey and M. Chaykovsky, *J.Am.Soc.*, 84, 867 (1962).
31. E.J. Corey and M. Chaykovsky, *J.Am.Soc.*, 84, 3782(1962).
32. E. Franzen and H.E. Driessen, *Chem.Ber.*, 96, 1881(1965).
33. E.J. Corey and M. Chaykovsky, *J.Am.Chem.Soc.*, 87, 1353 (1965).
34. B.M. Trost, *Account of Chem.Res.*, 7, 85 (1974).
35. H. Junjappa, *Synthesis*, 798 (1975).
36. E.T. Welski, J.L. Silver, M.D. Jansson and J.L. Burneister, *J.Org.Chem.*, 102, 365 (1975).
37. R.A. Abrnoviter and V. Alaxanian, *J.Org.Chem.*, 41, 2144 (1976).

38. L. Field and H.K. Chu, J.Org.Chem., 42, 1768 (1977).
39. W. Ando, Accounts of Chem.Res., 10, 179 (1977).
40. E. Block, Reactions of Organo Sulfur Compound, Academic Press, New York, pp 91, (1978).
41. D.C. Lankiu and H. Zimmer, Methodicum Chiumicum, 7B, 736 (1978).
42. J.I. Musher, Adv.Chem.Soc., 110, 44 (1972).
43. R. Hoffmann, J.M. Howell and E.L. Muetteries, J.Am.Chem. Soc., 94, 3047 (1972).
44. C.R. Jhonson, M. Hoake and C.W. Schroecls, J.Am.Chem. Soc., 92, 6594 (1970).
45. C.R. Jhonson and P.E. Rogers, J.Org.Chem., 38, 1793 (1972).
46. H. Schimidbaur and G. Kannel, Chem.Ber., 104, 3241(1971).
47. C.P. Lillya and P. Millor, J.Am.Soc., 88, 1559 (1966).
48. J. Adams, L. Hoffmann and B.M. Trost, J.Org.Chem., 35, 1600 (1970).
49. H. Konig and H. Metger, Chem.Ber., 98, 3733 (1965).
50. G. Seitz, Chem.Ber., 101, 585 (1968).
51. J. Tamura and J. Nishimura, J.Eiho and T.Miyamoto, Chem.Ind., 1199 (1971).
52. J. Tamura, T. Miyamoto, T. Nishimura & J. Kita, Tetrahedron Letters, 1199 (1971).

53. H. Schmidbaur and W. Kapp., Chem.Ber., 105, 1203(1972).
54. A.W. Jhonson, J.Org.Chem., 28, 252 (1963).
55. G. Wittig and H. Fritz, Amm., 517, 39 (1952).
56. V. Franzen and H.J. Schmidt and C. Mertz, Chem.Ber., 94, 2942 (1961).
57. K.W. Ratts, A.N. Rao and J.Org.Chem., 31, 1185 (1966).
58. V. Franzen and H.E. Driesson, Tetrahedron Letters, 661, (1962).
59. E.J. Corey and M. Chaykovsky, Tetrahedron Letters, 169, (1963).
60. A.W.JHonson, J.J. Hurby and T.K. Williams, J.Am.Chem. Soc., 86, 918 (1964).
61. E.D. Huges and K.I. Kuriyan, J.Chem.Soc., 1609 (1955).
62. H. Nazaki, K. Kondo and M. Takaku, Tetrahedron Letters, 257, (1965).
63. E.J. Corey and M. Chaykovsky, J.Am.Chem.Soc., 86, 1899 (1964).
64. A.J. Speziale, C.C. Tung, K.W. Ratts and A.N. Yao, J.Am.Chem.Soc., 89, 3460 (1965).
65. A.W. Jhonson and V.J. Hurby, J.Am.Chem.Soc., 84, 3586 (1962).
66. V. Franzen, H.L. Joschek and C. Mertz, Liebigs Am.Chem., 651, 82 (1962).

67. E.J. Corey and M. Jautelat, J.Am.Chem.Soc., 89, 3912 (1967).
68. A.W. Jhonson and R.T. Arnel, J.Org.Chem., 34, 1240 (1969).
69. H. Nozaki, D. Tunemoto, Z. Morita, K. Nakamura, K. Watanable, M. Takaku, K. Kondo, Tetrahedron, 20, 4279 (1967).
70. A.F. Cook and J.G. Maffat, J.Am.Chem.Soc., 90, 740 (1968).
71. D. Martin and H.J. Niclas, Chem.Ber., 102, 31 (1969).
72. S. Julia, C. Huynh and D. Michelot, Tetrahedron Letters, 3587 (1972).
73. W. Tllger, A. Liedhegener and M. Rigitz, Tustus Leiebig's, Am.Chem., 760, 1 (1972).
74. W. Ando, T. Yagihara, S. Tozume, J. Zrnai, J. Suzuki, T. Toyama, S. Nakaide and T. Migita, J.Org.Chem., 37, 1721 (1972).
75. C.R. Jhonson and W.G. Phillips, J.Org.Chem., 32, 1926 (1967).
76. H. Braun, G. Huber and G. Keszé, Tetrahedron Letters, 4033 (1973).
77. T. Shano, T. Akazawa and M. Mitani, Tetrahedron, 29, 817 (1973).

78. G. Markl and A. Merz, *Angew Chem., Int.Ed.*, 12, 845 (1973).
79. B.M. Trost, R.W. Larochille and M.J. Bogdanoviez, *Tetrahedron Letters*, 3449 (1970).
80. C.R. Johnson, A. Nakanishi, N. Nakanishi and K. Tanaka, *Tetrahedron Letters*, 2865 (1975).
81. C.R. Jhonson and K. Tanaka, *Synthesis*, 413 (1976).
82. B.M. Trost, *J.Amer.Chem.Soc.*, 89, 138 (1967).
83. B.M. Trost, *J.Amer.Chem.Soc.*, 88, 1587 (1967).
84. R.W. Larochille, B.M. Trost and L. Krepshi, *U.Org.Chem.*, 36, 1126 (1971).
85. E.J. Corey and M. Chaykovsky, *J.Am.Chem.Soc.*, 86, 1640 (1964).
86. A.W. Johnson and R.T. Arnel, *Tetrahedron Letters*, 819 (1966).
87. H. Nozaki, K. Nakamura and M. Takaku, *Tetrahydron*, 25, 3676 (1969).
88. P. Bravo, G. Zanodieno and A. Umanironchi, *Tetrahydron Letters*, 679 (1969).
89. P. Bravo, G. Zanodieno and M.G. Zubiani, *J.Hetracyclic Chem.*, 7, 967 (1970).
90. Y. Hayashi and R. Oda, *Tetrahedron Letters*, 853 (1969).

91. H. Machle, Tetrahydron, 19, 1159 (1963).
92. E.J. Corey and M. Chaykovsky, J.Am.Chem.Soc., 84, 3282 (1962).
93. A.W. Jhonson and V.J. Hurby, Abst.Papers 142nd meeting, Amer.Chem.Soc., p.310 (1967).
94. A.W. Jhonson and J.O. Martin, Chem. & Ind.(London), 1726 (1965).
95. E.J. Corey and W. Oppolozzer, J.Am.Chem.Soc., 86, 1899 (1964).
96. G.B. Payme, J.Org.Chem., 38, 3140 (1973).
97. F. Krollpfeiffer and H. Hautmann, Chem.Ber., 90 (1950).
98. G.B. Payme, J.Org.Chem., 32, 3337 (1967).
99. G.W. Krakower and H.A. Vandine, J.Org.Chem., 31, 3467 (1966).
100. T. Kunieda and B. Witkop, J.Am.Chem.Soc., 95, 3478(1971).
101. P.F. Torrence and B. Witkop, Biochemistry, 11, 1737 (1972).
102. A.G. Hortmann and D.A. Robertson, J.Am.Chem.Soc., 94, 2758 (1972).
103. V. Boekelheide and N.A. Fedoruk, J.Am.Chem.Soc., 90, 3830 (1968).

104. Y. Hayasi and H. Nozaki, Bull Chem.Soc., (Jpn), 45, 198 (1971).
105. T. Cohen, G. Hermann, J.M. Chapman and D. Kuhn, J.Am. Chem.Soc., 96, 5627 (1974).
106. T. Thomson and T.S. Stevens, J.Chem.Soc., 69 (1932).
107. C.R. Houser, S.W. Kantor and W.R. Brasen, J.Am.Chem. Soc., 75, 2660 (1953).
108. G. Andrew and D.A. Evans, Tetrahedron Letters, 512(1972).
109. J. Tanimoto, J. Horikawa and R. Oda, Kogyo Kagaku, Zasshi, 70, 1969 (1967).
110. S. Tanimoto, J. Horikawa and O. Oda, Yuki Gosei, Kagaku Kyokai Sh., 27, 899 (1969).
111. M. Senga, S. Kondo and K. Tsuda, J. Polym Sci.Polym. Lett.Ed., 20, 657 (1982).
112. H.C. Hass and R.D. Moreau, Ibid., 15, 1225 (1977).
113. M.J. Farrall, T. Durst and J.M.J. Frechet, Tetrahedron Letters, 203 (1979).

CHAPTER II

CHAPTER-II

SYNTHESIS OF 1,3,5-TRISUBSTITUTED NAPHTHALENES USING NON STABILIZED π -SULFURANES : REACTION OF O-SUBSTITUTED BENZYL DIMETHYL SULFONIUM BROMIDES WITH α , β -UNSATURATED KETONES.

II.1. ABSTRACT :

O-chlorobenzyl dimethyl sulfonium bromide, O-bromobenzyl dimethyl sulfonium bromide and O-nitrobenzyl dimethyl sulfonium bromide have been prepared by the reaction of O-chlorobenzyl bromide, O-bromobenzyl bromide and O-nitrobenzyl bromide with dimethyl sulfide in benzene in an atmosphere of nitrogen at reflux temperature in fair to good yields. These sulfonium salts on reaction with base generated corresponding O-substituted benzylidene dimethyl sulfuranes in situ. The reaction of these salts or sulfuranes with a wide range of substituted benzylidene acetophenones in presence of anhydrous aluminium chloride or zinc chloride in the mixture of ammonium acetate and acetic acid gave 1,3,5-triarylnaphthalenes in good yields. Aluminium chloride or zinc chloride in acetic acid is used as cyclization agent. The structures of naphthalene derivatives were confirmed by elemental analysis, IR and NMR spectral data.

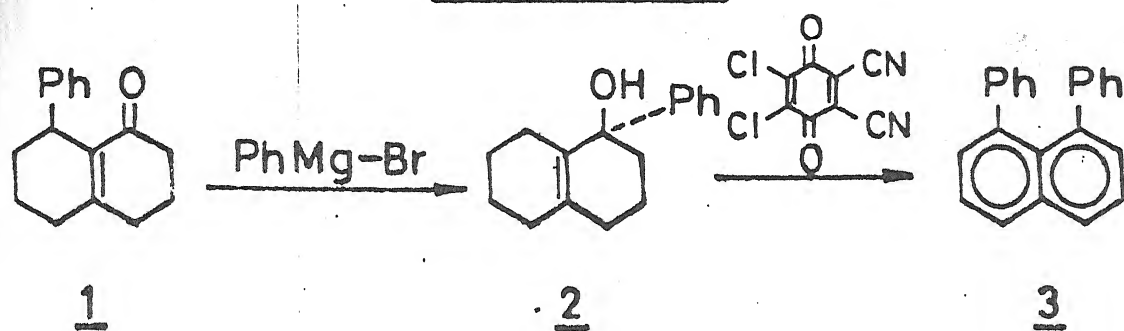
II.2. INTRODUCTION :

The various methods reported for the synthesis involved several steps and the yields of the final product was also poor. The house et al¹⁻² were the first who attempted to prepare

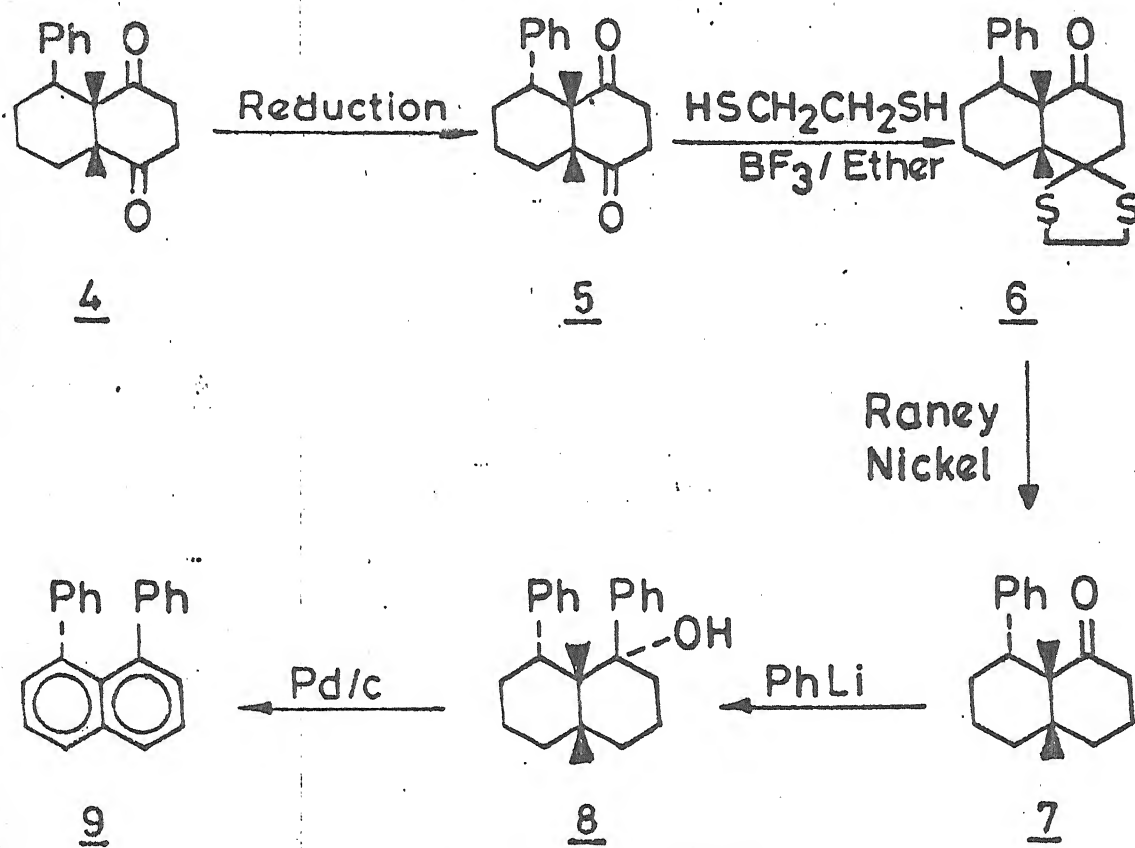
naphthalene derivatives by the reaction of 8-phenyl Δ^{1-10} -octal-1-one (1) with phenyl magnesium bromide to form an alcohol (2), which underwent dehydrogenation and dehydration with 2,3-dichloro-5,6-dicyanobenzoquinone in boiling benzene to afford to give desired product (3) (Scheme II.1). Since the route involved harsh reaction conditions and yields of the final product was also very poor. Bailey et al³ reported another route which involved several steps for the synthesis of 1,8-dimethyl naphthalene (9) according to this synthesis first the reduction of 1,4,5,8,9,10-hexahydro-1,4-dioxo-5-phenylnaphthalene (4) took place. The resulting product (5) thioketals (6) with ethanol thio desulphurization with Raney nickel and the subsequent treatment of the resulting product (7) with phenyl lithium to give 1-transhydroxy -cis-syn-1,8-diphenyl decaline (8) were carried out. The product (8) on dehydrogenation with Pd/C carbon gave 1,8-diphenyl naphthalene (9) (Scheme II.2).

Later on a convenient and facile route was reported by Krohnke et al⁴ for the synthesis of diaryl naphthalene derivatives which involved the condensation of benzylpyridinium bromide (10) with benzal acetophenone (11). In presence of zinc chloride to give 1,3-diphenyl naphthalene (12) (Scheme II.3). This Krohnke's⁴ method proved better than aforesaid mention methods because it involved single step and gave better yields of final product. Later on Tewari et al⁵ and Gupta et al⁶ also duplicated the reaction and reported the detail experimental

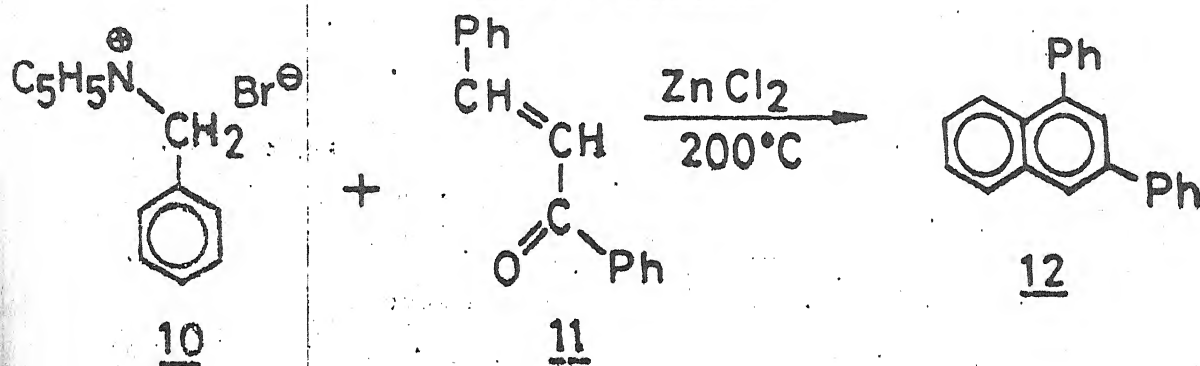
Scheme II. 1.



Scheme II-2



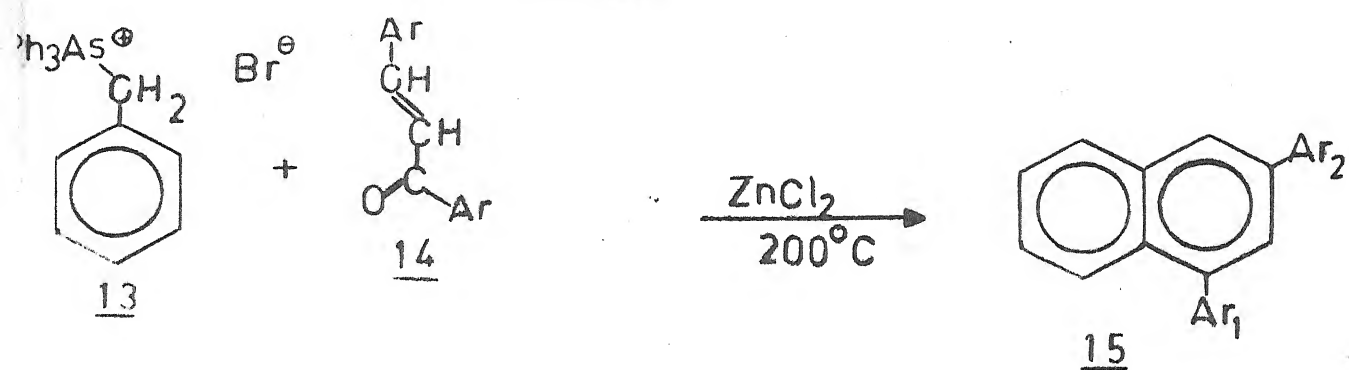
Scheme II.3



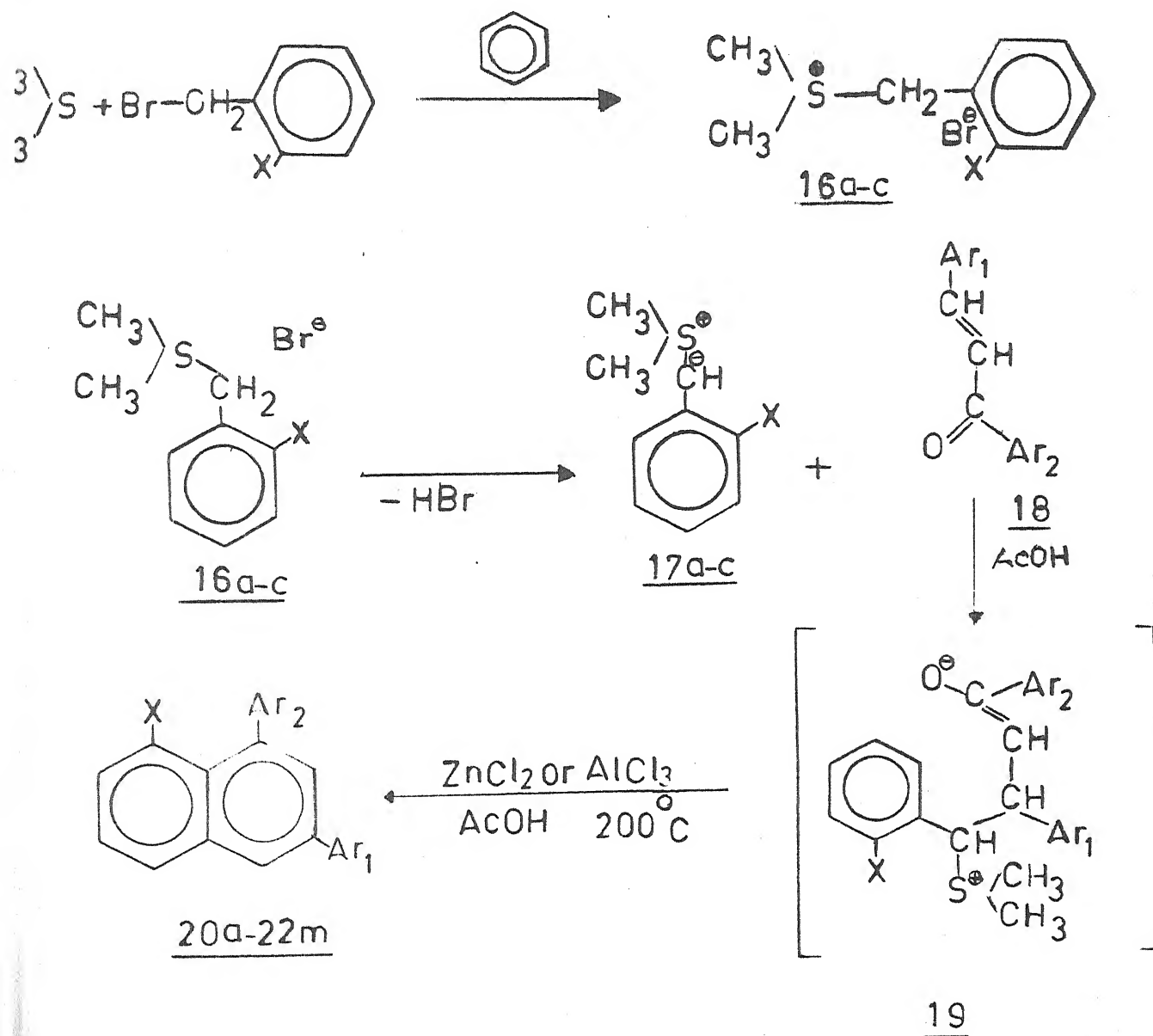
conditions for the preparation of 1,3-diaryl naphthalene. Further more, this reaction selective introduction of substituents at 1 and 5 positions of the naphthalene nucleus. However a few reactions following this procedure have been reported but detailed experimental conditions have not been described. Prompted from this work seemed to be of great interest to explore the domain of applicability of this new route.

Subsequently Gupta et al⁷ have synthesized naphthalene nucleus (15) by the use of phenacyltriphenylarsonium salts (13) with α, β -unsaturated ketones (14) in presence of anhydrous zinc chloride in the mixture of sodium acetate and glacial acetic acid. The course of reaction of arsonium salts was also found to similar to that of corresponding pyridinium salts reported earlier 5,6 (Scheme II.4).

The pyridinium⁶ and arsonium salts⁷ were successfully utilized in the synthesis of naphthalene nucleus as reported earlier. It was therefore thought worthwhile to investigate an alternative route for the synthesis of naphthalene derivatives which the reaction of sulfonium salts with α, β -unsaturated ketones with view to compare the course of reaction of sulfonium salt and corresponding sulfonium ylides with these of analogous pyridinium and arsonium salts and corresponding ylides of V group elements.



Scheme II.5



II.3. RESULTS & DISCUSSION :

The reaction of O-chlorobenzyl bromide, O-bromobenzyl bromide and O-nitrobenzyl bromide with dimethyl sulphide in benzene at reflux temperature under nitrogen atmosphere gave O-chlorobenzyl dimethyl sulfonium bromide (16a), O-bromobenzyl dimethyl sulfonium bromide (16b) and O-nitrobenzyl dimethyl sulfonium bromide (16c) (Scheme II.5).

The structures of these sulfonium salts (16 a-c) were evidenced on the basis of IR and NMR data. The IR spectra of these salts showed characteristic absorption bands of strong intensity at, 3045 cm^{-1} , 3040 cm^{-1} and 3000 cm^{-1} and 3060 cm^{-1} respectively due to C-H stretching vibration bands of methylene group attached to a position adjacent to S-atom. This diagnostic absorption band due to nitro group in the salt (16c) were obtained at 1520 cm^{-1} , 1300 cm^{-1} . The NMR spectra of (16 a-c) showed a strong singlet in the range $\delta 5.0-5.3$ due to methylene group attached to the sulfonium group. A sharp singlet at $\delta 3.0-3.2$ were due to two methyl groups directly attached to sulfonium group and aromatic protons were observed in the range $\delta 7.05-8.45$.

The reaction of these salts (16 a-c) were carried out with a wide range of α,β -unsaturated carbonyl compounds in presence of anhydrous aluminium chloride or zinc chloride in a mixture of sodium acetate and acetic acid at 200°C to afford 1,3-diaryl-5-chloro naphthalenes (20 a-m), 1,3-diaryl-5-bromo

naphthalenes (21 a-m) and 1,3-diaryl-5-nitronaphthalenes (22a-m) in 50-75% yields. It was however, observed that the yields of resulting naphthalenes were dependent upon the nature of substituents attached to sulfonium salts (16a-c) as well as to the α - β -unsaturated ketones. The reactivity of salt (16c) was lower than salts (16a-b) because of -I effect of NO_2 which stabilized the carbanion formation. Hence, salt (16c) afforded lower yields of naphthalene derivatives than the salt (16a-b).

The reaction seems to proceed via the intermediates of a betaine type of derivatives (19), which is formed by the nucleophilic attack of the ylide carbons (17a-c) presumably generated in situ by dehydrohalogenation of salts (16a-c), on the β carbon of α , β -unsaturated ketones (18), betaine (19), then undergoes cyclization in presence of anhydrous zinc chloride or aluminium chloride used as cyclization agent to afford naphthalene derivatives (20a-22m) obtained in the present investigation were crystalline solids usually soluble in chloroform, dimethyl sulfide and acetone. All physical data have been reported in table II.1. All the compounds are new and gave satisfactory elemental analysis. The IR spectral⁸ data (table II.2) of naphthalene derivatives showed a double absorption maxima in the region $1630\text{-}1620\text{ cm}^{-1}$ which were assigned to the stretching vibrations of carbon-carbon double bond. The strong bands in the region $900\text{-}850\text{ cm}^{-1}$ were diagnostic absorption of polynuclear aromatics. The nitro group of the

products showed a strong symmetrical stretching band at 1350-1330 cm^{-1} . The NMR spectra of compound in general, exhibited aromatic multiplet in the range δ 6.50-8.50 methyl protons at δ 2.25-2.30 and methoxy protons at δ 3.75-3.80.

II.4. EXPERIMENTAL :

II.4.1. General techniques :

Until and unless not specified, here and hereinafter melting points were recorded in degrees centigrade on a Gallen Kamp apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer infracord spectrophotometer using KBr phase. Varian A-60 and A-100 spectrometer was used to record NMR spectra using tetramethylsilane (TMS) as an internal standard. The products were separated and purified by column chromatography using neutral alumina as absorbent. Glass microscope slides coated with silica gel G were used for thin layer chromatography (TLC). The spots on slides were developed by placing them in iodine chamber.

II.4.2. Starting materials :

All the reagents were obtained from commercial sources i.e. B.D.H., S. Merck, E. Merck etc. The starting materials were prepared according to references cited. Thus O-chlorobenzyl bromide, O-bromobenzyl bromide and O-nitrobenzyl bromide were prepared by the direct bromination of corresponding O-substituted

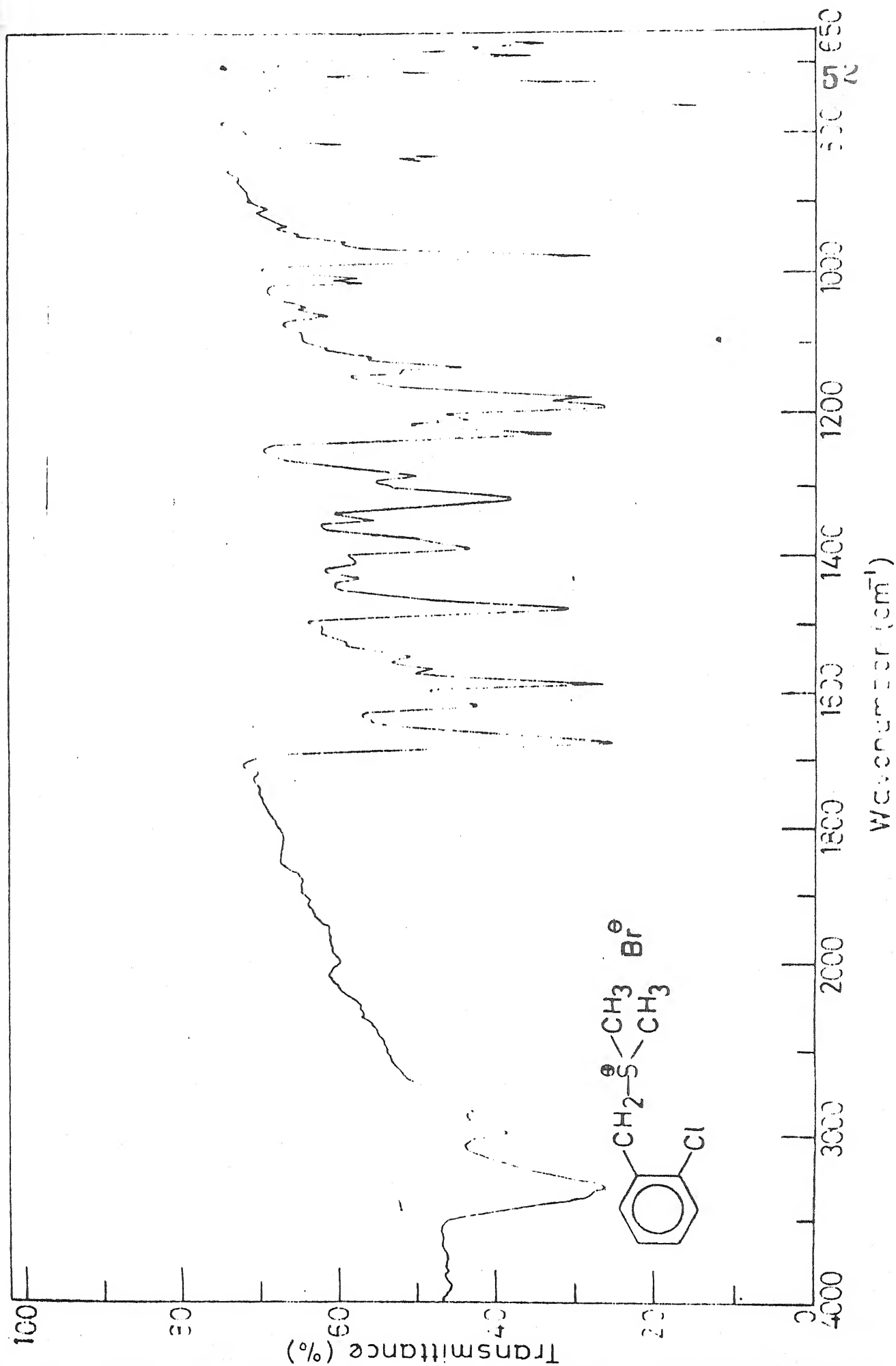


FIG. II.1.1 IR SPECTRUM OF 16a.

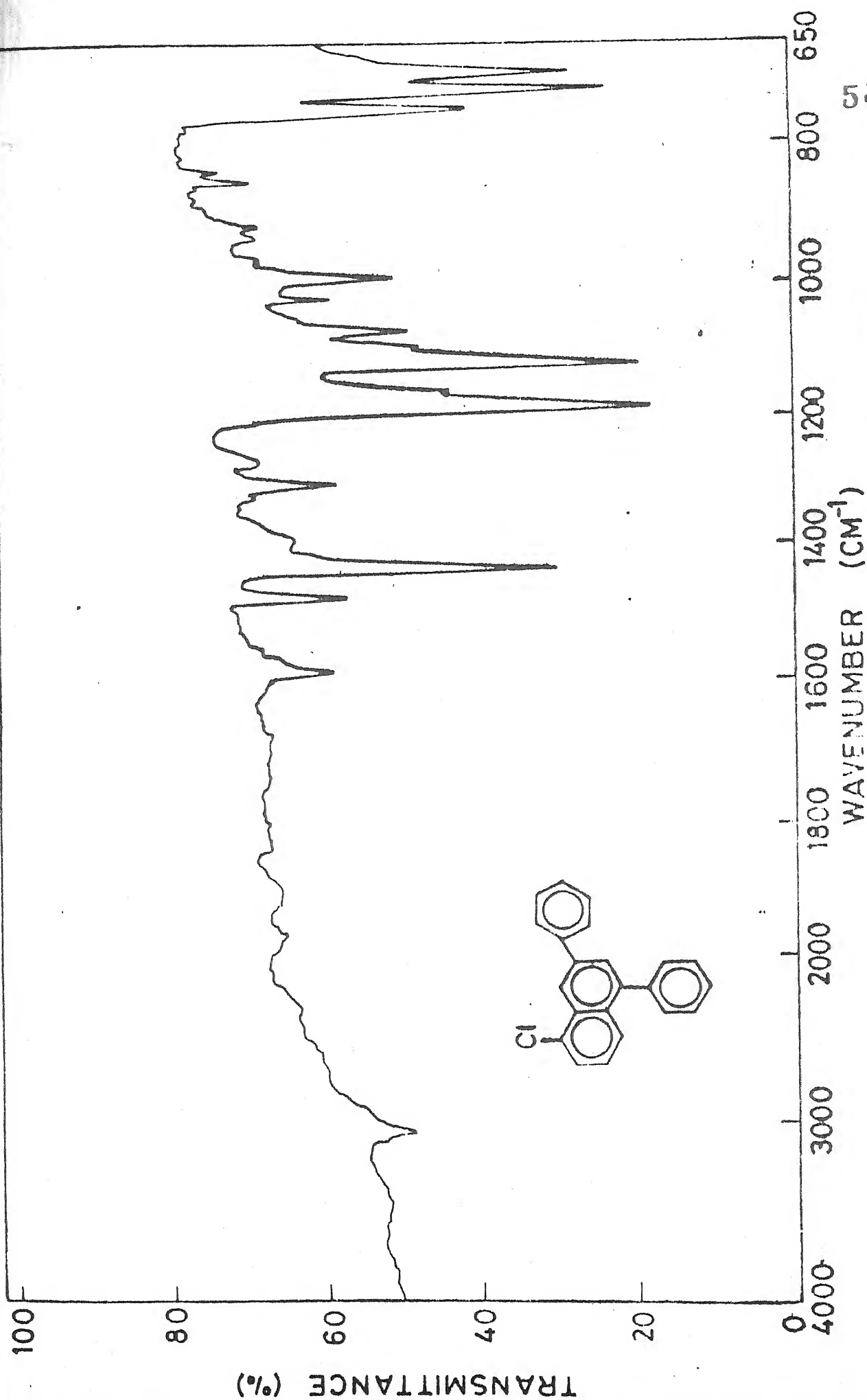


FIG. 11-2 IR SPECTRUM OF COMPOUND (200a)

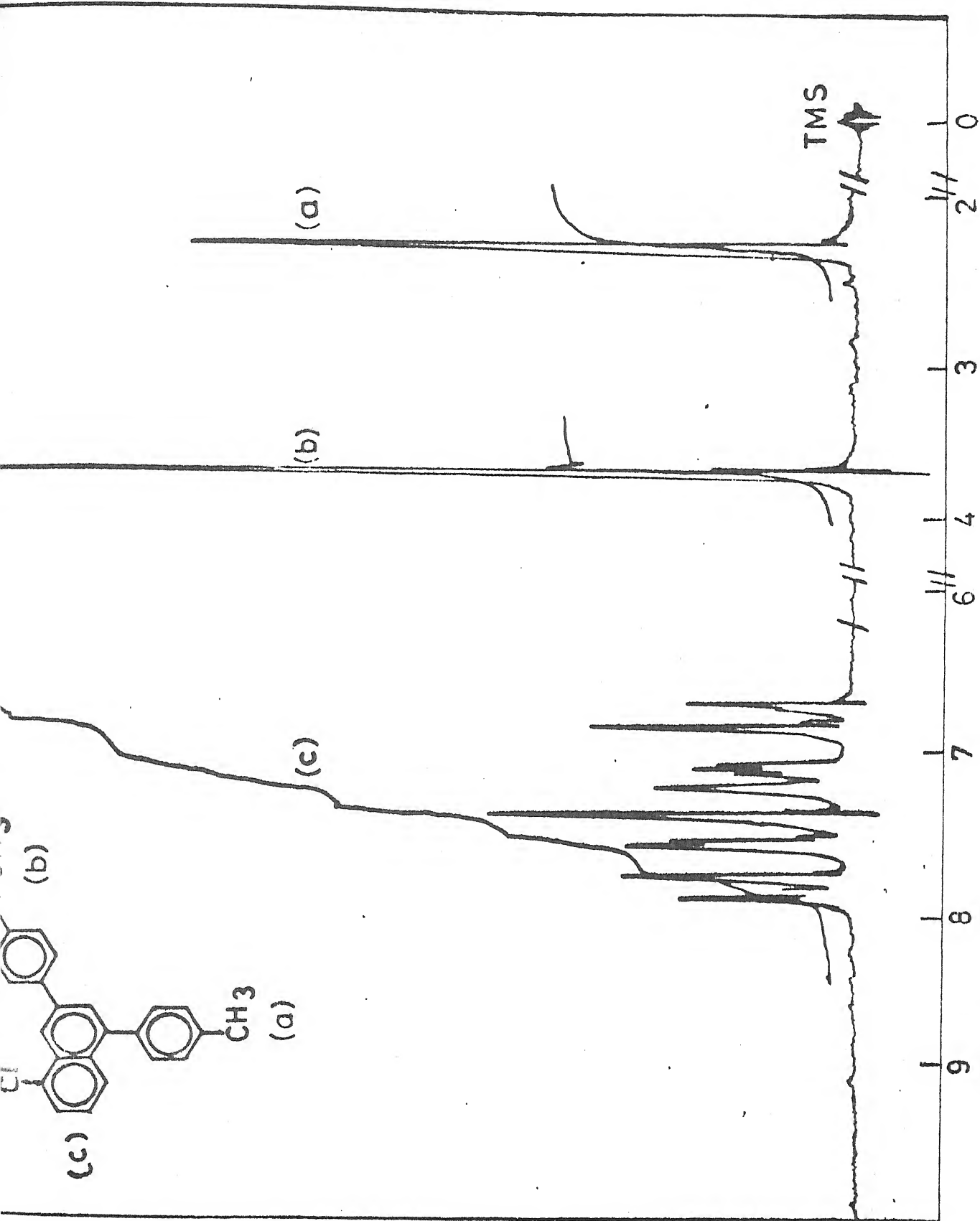


FIG. II · 3 NMR SPECTRUM OF COMPOUND (20g)

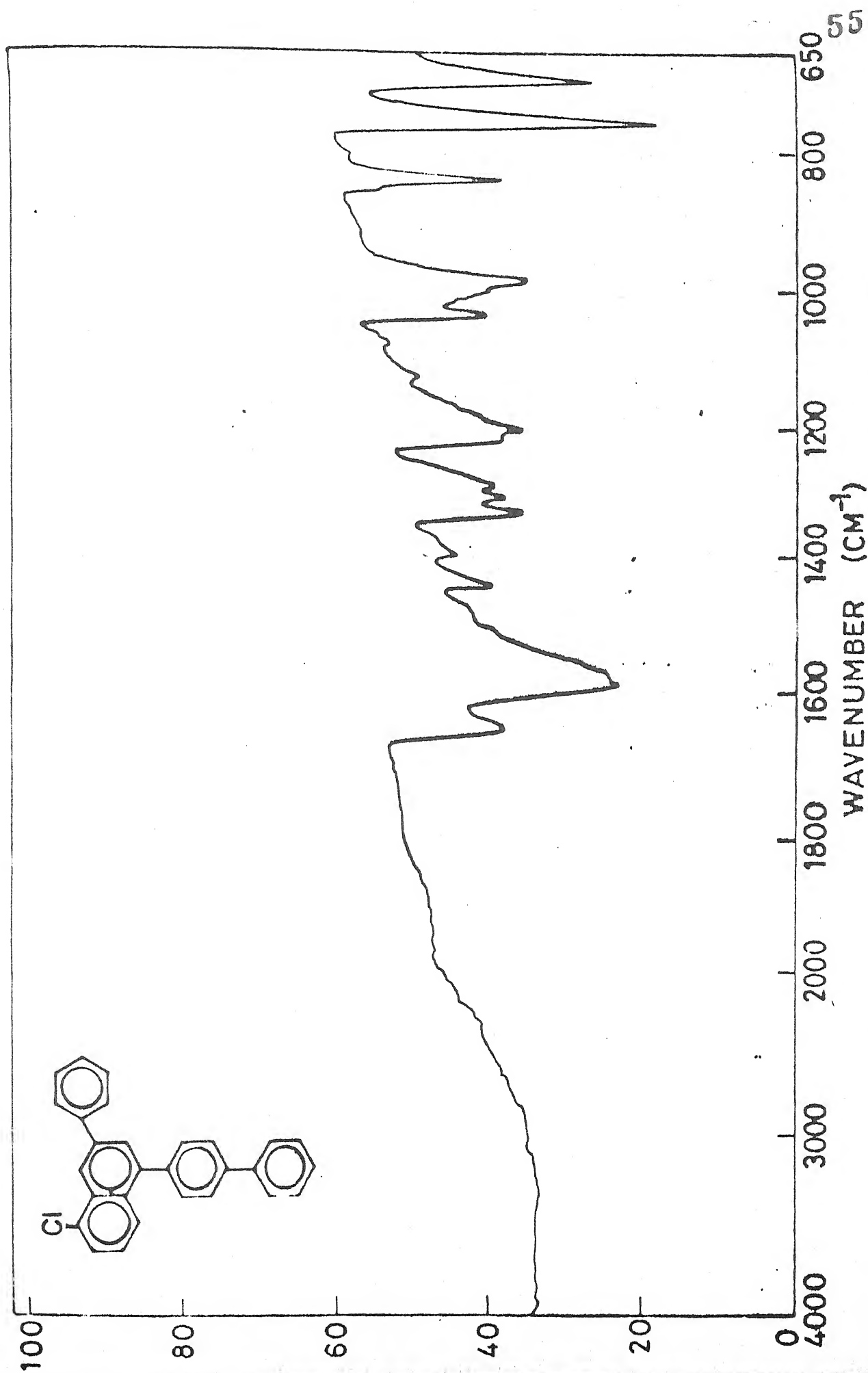


FIG II.4. IR SPECTRUM OF COMPOUND (201)

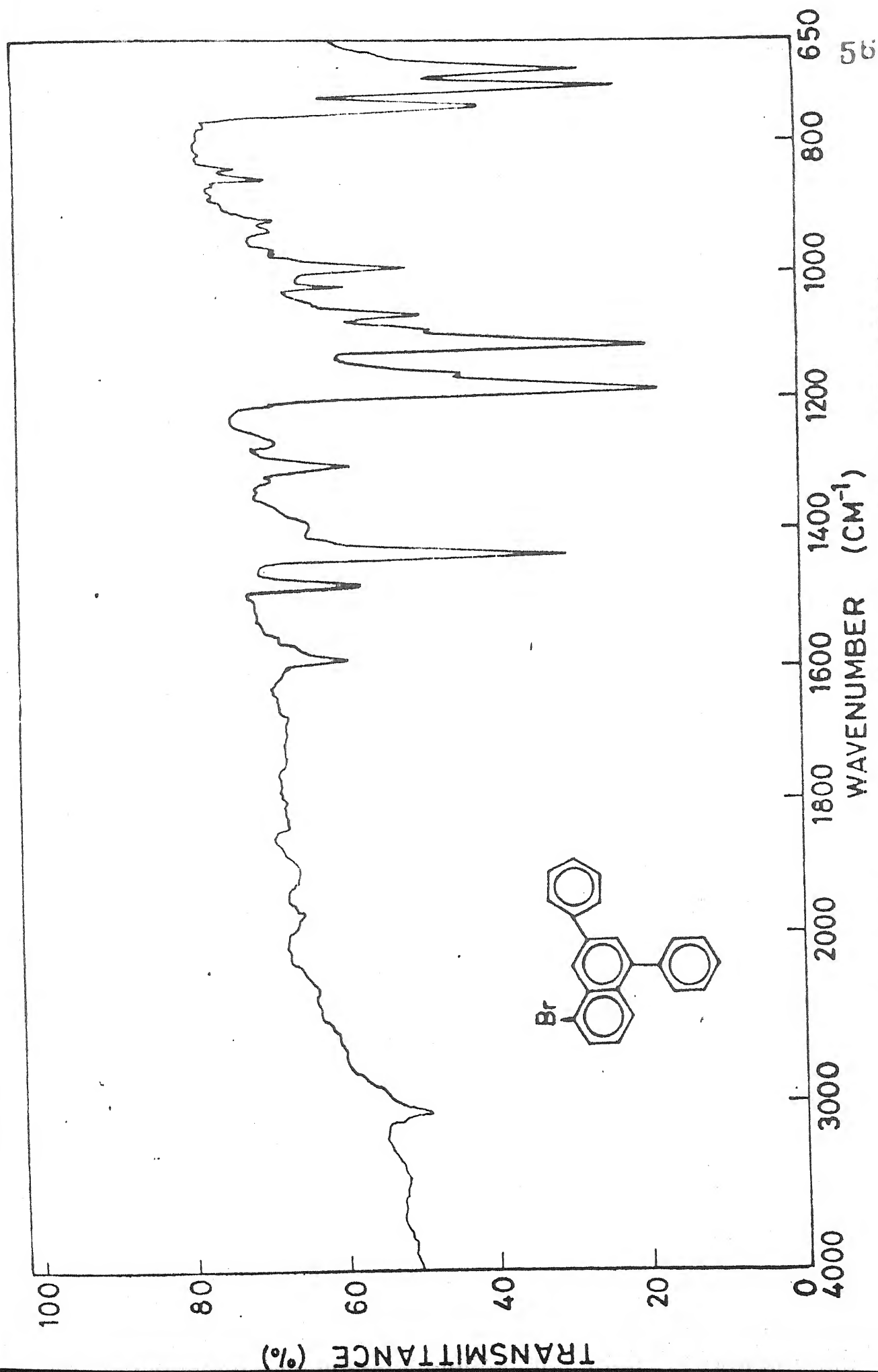


FIG. 11 · 5 IR SPECTRUM OF COMPOUND (21a)

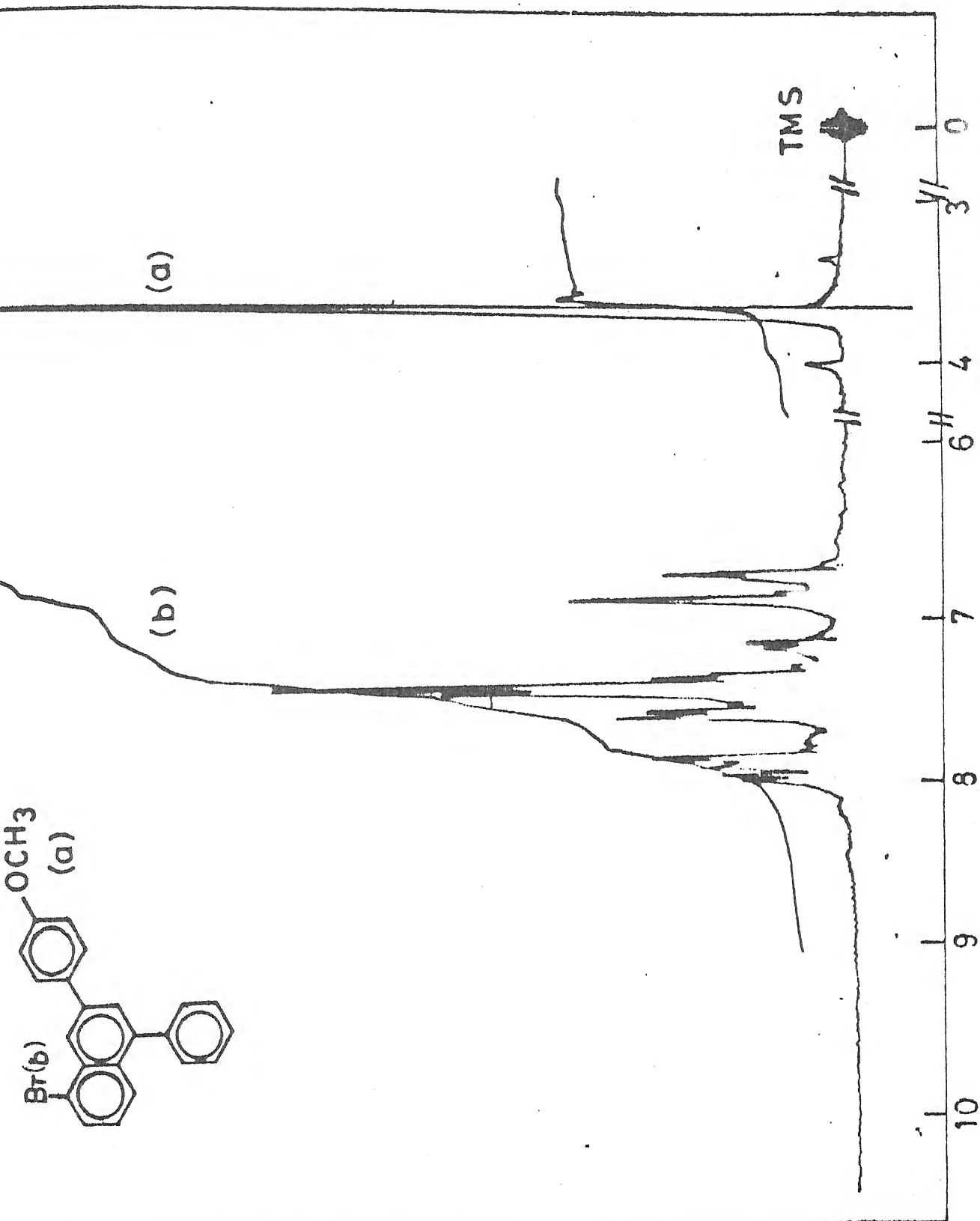


FIG. II.5 NMR SPECTRUM OF COMPOUND (21c)

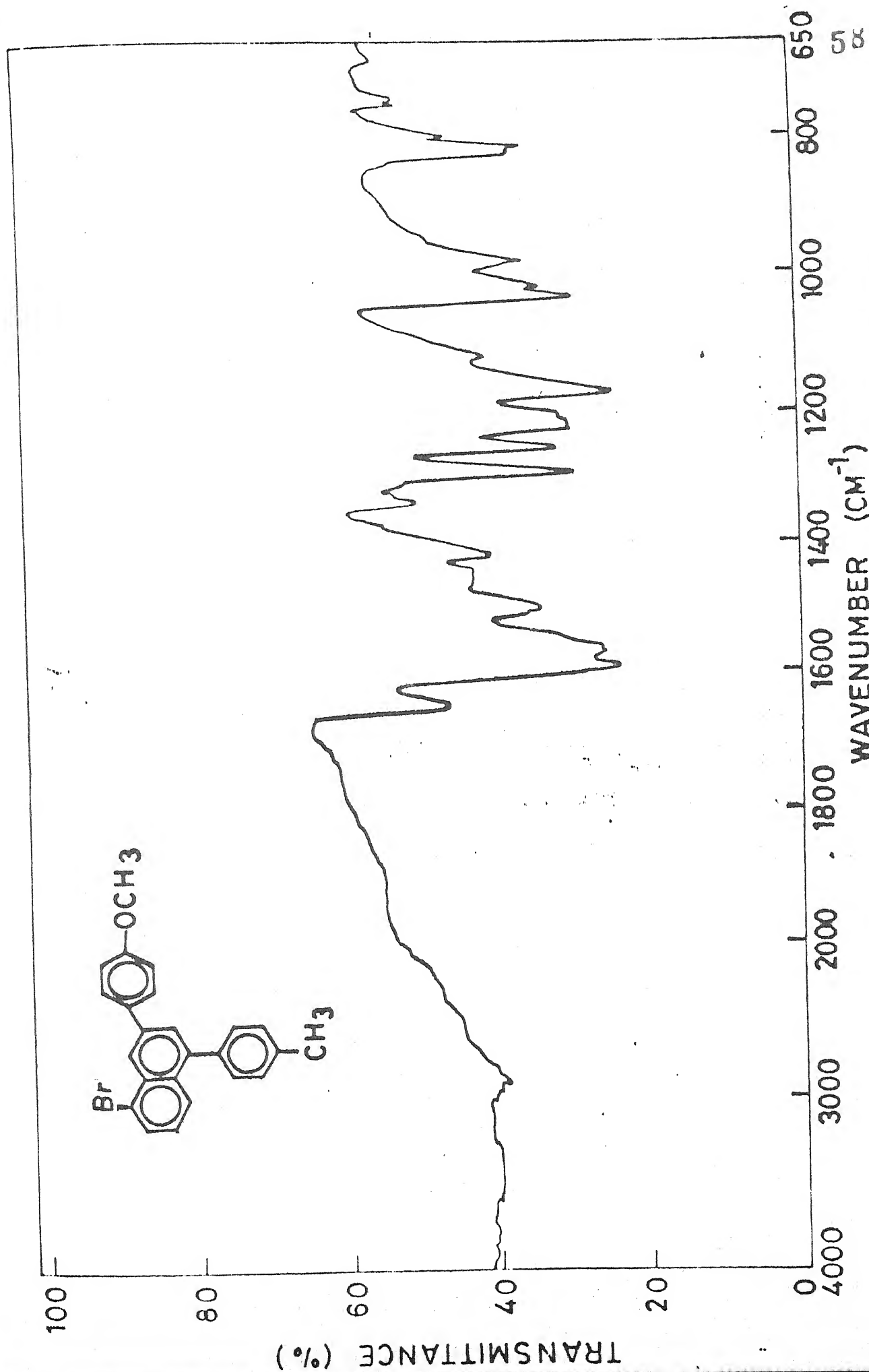


FIG II.7 IR SPECTRUM OF COMPOUND (219)

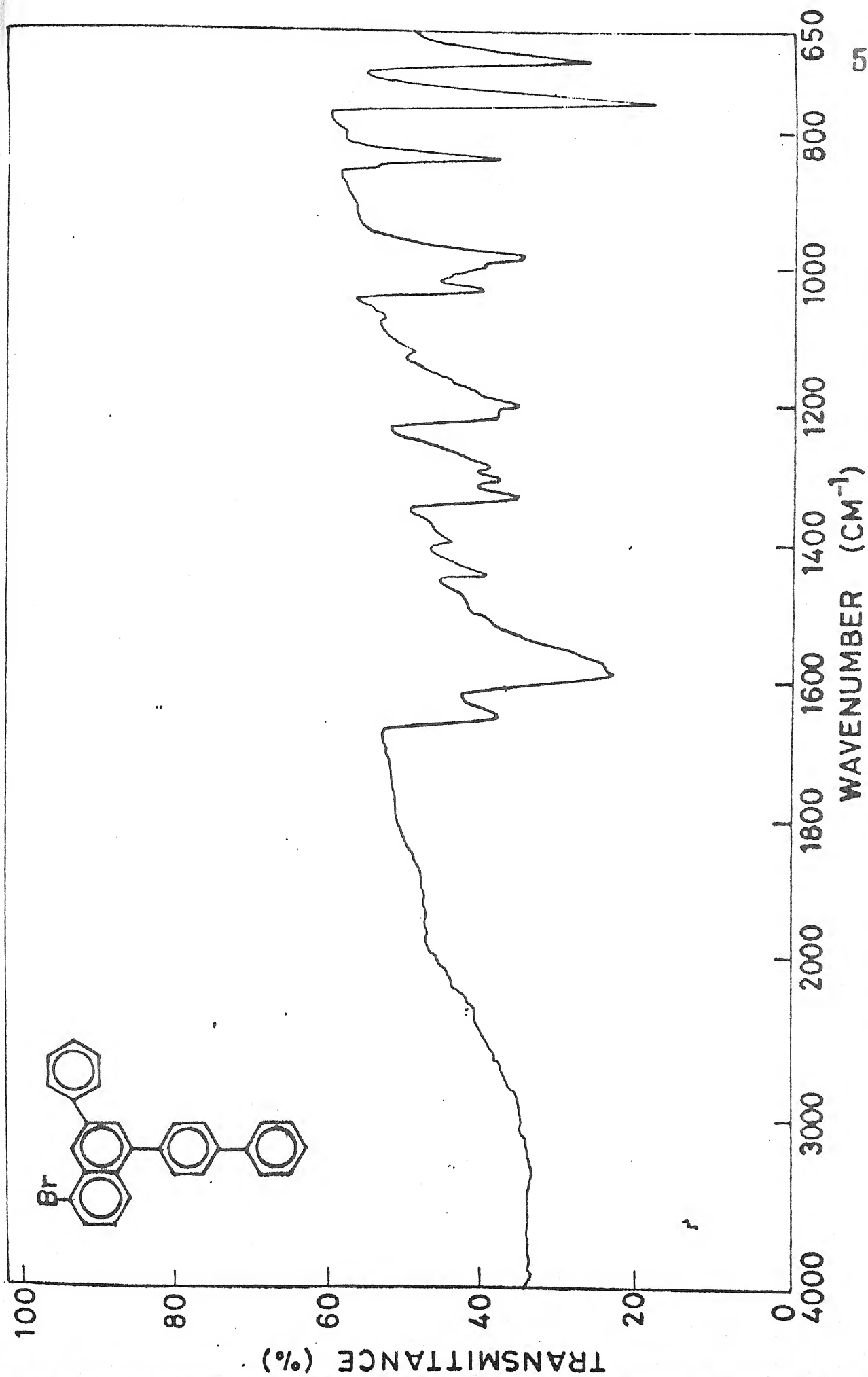


FIG. II · 8 IR SPECTRUM OF COMPOUND (211)

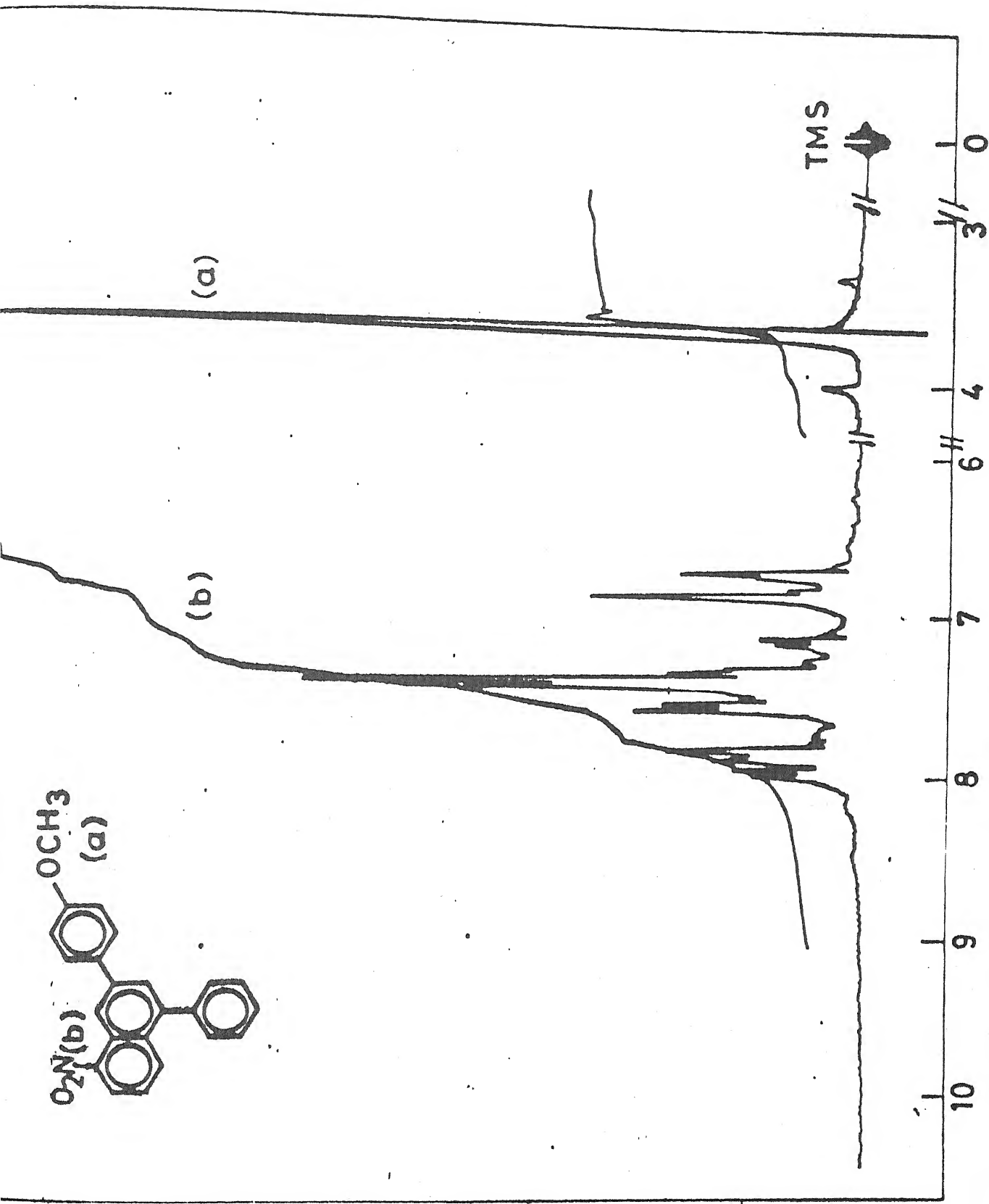
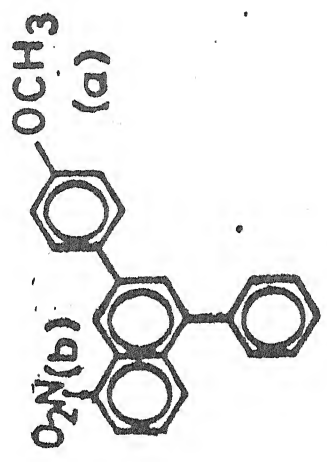


FIG. 11: 9 NMP SPECTRUM OF COMPOUND (22C)



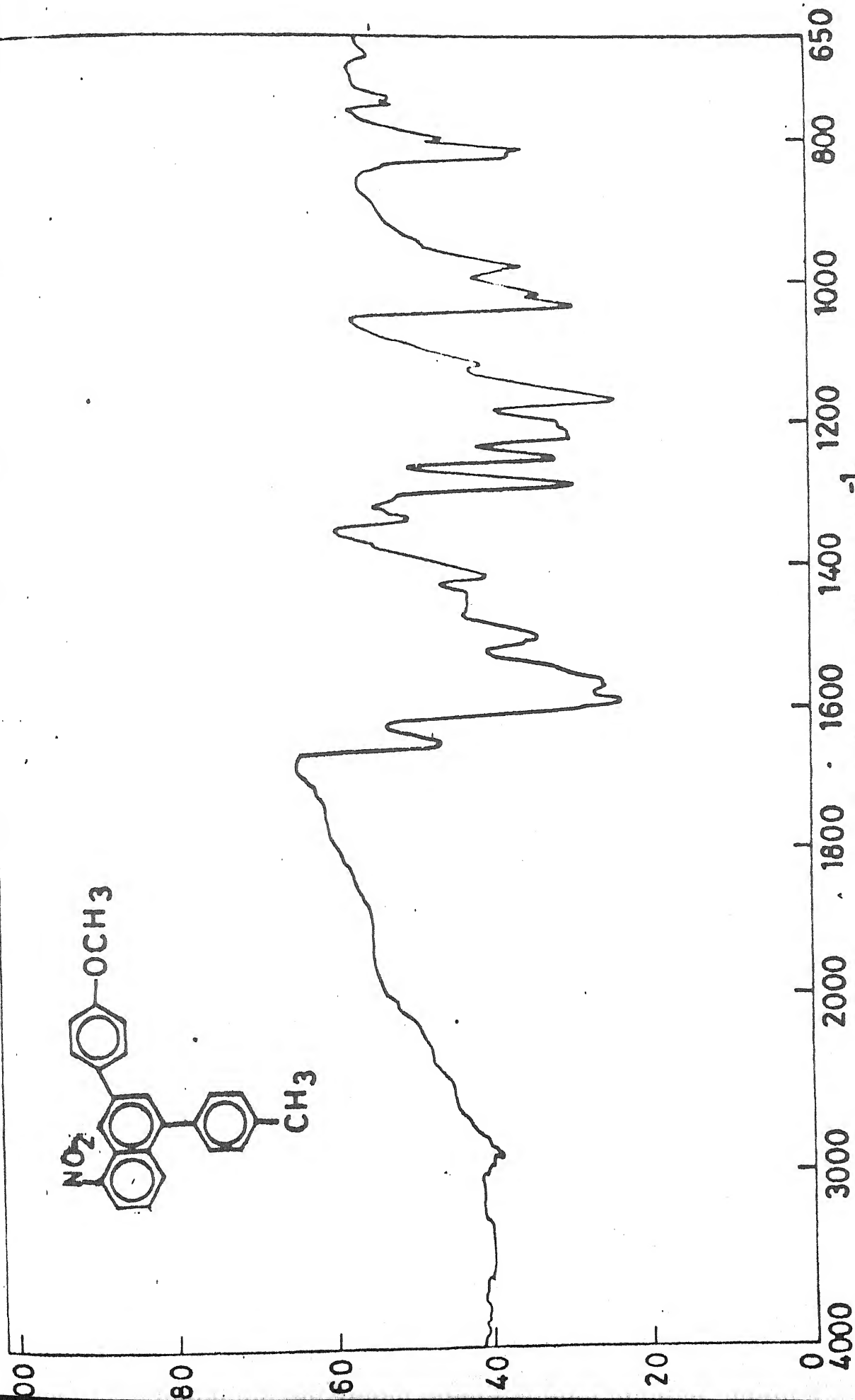


FIG. II. IR SPECTRUM OF COMPOUND (22g)

toluenes at elevated temperatures^{10,11}.

The substituted benzylideneacetophenones (18) were prepared by a general procedure¹². This method consists of stirring the equimolar quantities of aromatic aldehydes and methyl ketones in the presence of an alkali at 0°C. The resulting precipitate of α, β -unsaturated ketones was recrystallized from ethanol by benzene: Pet. ether (60-80°C) in 40-80% yields.

II.4.3. Preparation of O-chlorobenzyl dimethyl sulfonium bromide (16a) :

A solution of dimethyl sulfide (50 m mole) and O-chlorobenzyl bromide (50m mole) in 50 ml of anhydrous benzene was allowed to reflux on a water bath for 4 hrs. A solid mass was precipitated which was filtered, dried and recrystallized twice from chloroform, n-hexane to give white shining crystals of O-chlorobenzyl sulfonium bromide in 80% yields (11.50 gm) m.p. 150-151°C (Lit¹³ m.p. 150-152°C).

IR data (KBr) cm^{-1} : 3045 (δ C-H to $\text{CH}_2\text{-S}^+\text{<}$)

NMR (CDCl_3) (δ ppm) : 5.10 (s, 2H, $\text{-CH}_2\text{-S}^+\text{<}$) :

3.05 (s, 6H, di CH_3), 7.05-8.25 (m, 4H, ArH)

II.4.4. Preparation of O-bromobenzyl dimethyl sulfonium bromide (16b) :

O-bromobenzyl bromide (50m mole) and dimethyl sulfide

(50m mole) in anhydrous benzene (50 ml) was allowed to reflux on a water bath for 6 to 7 hrs. A solid mass was precipitated, which was filtered, dried and recrystallized twice from chloroform, n -hexane to give off white crystals of O-bromo-benzyl dimethyl sulfonium bromide (16b) in 75% yields.

m.p. 142-44°C (Lit¹³ 144-145°C)

IR data (KBr) cm^{-1} : 3040 (ν C-H to $-\text{CH}_2-\text{S}^+<$)

NMR (CDCl_3) (δ ppm) : 5.05 (s, 2H, $\text{CH}_2-\text{S}^+<$)

3.00 (s, 6H, di CH_3) : 7.15-8.30 (m, 4H, ArH)

II.4.5. Preparation of O-nitrobenzyl dimethyl sulfonium bromide (16c) :

A mixture containing (50m mole) of O-nitrobenzyl bromide and (50m mole) dimethyl sulfide in 50ml of anhydrous benzene was heated on a water bath for 8-10 hrs. Excess of solvent was evaporated and Pet. ether (60-80) was added to precipitate O-nitrobenzyl dimethyl sulfonium bromide (16c). This salt (16c) was twice crystallized from chloroform, n -hexane (1:2) to give a yellow crystalline compound m.p. 158-60°C (Lit¹⁴ m.p. 155-60°C) yields 26.5 gm (90%).

IR data (KBr) cm^{-1} : 3040 (ν C-H to $\text{CH}_2-\text{S}^+<$),

1520, 1300 (ν - NO_2)

NMR (CDCl_3) (δ ppm) : 5.30 (s, 2H, $\text{CH}_2-\text{S}^+<$)

3.20 (s, 6H, di CH_3) : 7.05-8.40 (m, 4H, ArH)

II.4.6. Preparation of 1,3-diaryl-5-chloronaphthalenes
(20a-m) :

A mixture of O-chlorobenzyl dimethyl sulfonium bromide (16a) (3m mole) and α, β -unsaturated ketones (3m mole) was stirred at 200°C in the presence of anhydrous zinc chloride (3.0g) in 10ml glacial acetic acid for 6-9 hrs under nitrogen atmosphere. Reaction mixture, after keeping overnight at room temperature into ice cold water (20ml) to precipitate a solid mass. The solid mass was separated by filtration, dried and subjected to column chromatography using neutral alumina as absorbent and chloroform as solvent. The products were recrystallized from suitable solvents to give better yields of the titled compounds (20a-m). Table (II.1). The NMR and IR spectral data of naphthalenes (20a-m) have been tabulated in table II 2-3.

II.4.7. Preparation of 1,3-diaryl-5-bromonaphthalenes
(21a-m) :

Taking the (3m mole) solution of O-bromobenzyl dimethyl sulfonium bromide (16b) in a 100ml round bottom flask and equipped with a reflux condenser with magnetic stirrer and α, β -unsaturated ketones in 5.0ml of glacial acetic acid followed by the addition of 3.0gm anhydrous zinc chloride. The mixture was stirred at 200°C for 6-8 hrs under an inert atmosphere of nitrogen. The resulting solution was allowed to stand overnight at room temperature. Ice cold water (20ml) was then added, the

precipitate so obtained was filtered off, dried and chromatographed over neutral alumina chloroform fraction which on crystallization from an appropriate solvent gave a fine crystalline solid due to formation of 1,3-diaryl O-bromonaphthalenes (21a-m).

All the naphthalene derivatives (21a-m) were prepared using the same general procedure. Their physical constants are listed in table II.1-3.

II.4.8. Preparation of 1,3-diaryl-5-nitronaphthalenes (22a-m) :

In a 100ml round bottom flask, equipped with a reflux condenser and a magnetic stirrer, was placed with a solution of O-nitrobenzyl dimethyl sulfonium bromide (16c) (3m mole) and α, β -unsaturated ketones in 5.0ml of glacial acetic acid followed by the addition of 3.0gm anhydrous zinc chloride. The mixture was stirred at 200°C for 7-9 hrs under an inert atmosphere of nitrogen. The resulting solution was allowed to stand over night at room temperature. Ice cold water (20ml) was then added. The precipitate so obtained, was filtered off, dried and chromatographed over neutral alumina chloroform fraction which on crystallization from an appropriate solvent gave an appropriate solvent gave a fine crystalline solid due to formation of 1,3-diaryl-O-nitronaphthalenes (22a-m).

All the naphthalenes derivatives (20a-22m) were

prepared using the same general procedure. Their physical constants are listed in table II.1-3.

REFERENCES

1. H.O. House, R.W. Magin and H.W. Thompson, J.Org.Chem., 28, 2403 (1963).
2. H.O. House and R.W. Boshe, J.Org.Chem., 30, 2942 (1965); 32, 784 (1967).
3. A.S. Beilley, G.A. Dale and J.A. Shuttleworth and D.P. Weizmann.
4. F. Krohnke and W. Zecher, Angew.Chem.Int.Ed.1, 626(1962).
5. R.S. Tewari and D.K. Nagpal, Tetrahedron Letters 569, (1976).
6. K.C. Gupta, B.K. Saxena, P.K. Pathak and N. Srivastava, Current Sci.,54, 571 (1985).
7. K.C. Gupta, P.K. Pathak & B.K. Saxena, Indian J.Chem. 24B, 783 (1985).
8. L.J. Belammy "Infrared spectra of complex molecules" John Wiley and Sons, New York, p.p.271 (1954).
9. R.M. Silverstein and G.C. Basseler, "Spectroscopic Identification of Organic Compounds", John Wiley and Sons, New York, p.p.49 (1963).
10. G.H. Jones, M.S. Kharasch, E.T. Margolis, P.C. White and F.R. Mayo, J.Amer.Chem.Soc., 59, 1405 (1954).
11. A.L. Vogel, "A Text book of Practical Organic Chemistry", Longman, p.p.961 (1948).

12. H. Gilmann and A.H. Blatt, "Organic synthesis", John Wiley and Sons, New York, Coll.Vol.1, p.p.78, (1958).
13. A.W. Jhonson and R.T. Arnel, J.Org.Chem., 34, 1240 (1969).
14. K.W. Ratts and A.N. Rao, J.Org.Chem., 31, 1185 (1966).

TABLE II.1. PHYSICAL PROPERTIES OF NAPHTHALENES DE IVATIVES (20a-22m)

| Compound | X | Ar ¹ | Ar ² | Yield % | m.p. °C | Lit. m.p. °C | Recry- stn. solvent | Anal. data found/(Calcd.) C % | H % |
|----------|----|--|---|---------|------------|--------------------|---------------------------|----------------------------------|----------------|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| 20a | Cl | C ₆ H ₅ | C ₆ H ₅ | 50 | 92-94 | 94-96 | B | 83.82 (83.94) | 4.83 (4.77) |
| b | Cl | C ₆ H ₅ | 4-CH ₃ C ₆ H ₄ | 50 | 109-11 | 108-10 | C | 84.04 (84.02) | 5.14 (5.18) |
| c | Cl | C ₆ H ₅ | 4-CH ₃ OC ₆ H ₄ | 54 | 124-26 | 125-27 | A | 80.18 (80.12) | 4.82 (4.93) |
| d | Cl | C ₆ H ₅ | 4-Cl.C ₆ H ₄ | 56 | 108-10 | 110-12 | C | 75.61 (75.64) | 4.07 (4.01) |
| e | Cl | C ₆ H ₅ | 3,4-O ₂ CH ₂ .C ₆ H ₃ | 55 | 134-36 | 133-35 | C | 77.38 (74.42) | 3.70 (3.65) |
| f | Cl | 4-CH ₃ .C ₆ H ₄ | C ₆ H ₅ | 67 | 120-21 | 121-22 | A | 84.05 (84.02) | 5.06 (5.14) |
| g | Cl | 4-CH ₃ .C ₆ H ₄ | 4-CH ₃ O.C ₆ H ₄ | 52 | 96-98 | 95-97 | B | 80.28 (80.33) | 5.32 (5.30) |
| h | Cl | 4-Cl.C ₆ H ₄ | 4-NO ₂ .C ₆ H ₄ | 55 | 192-94 | 190-91 | B | 69.90 (69.84) | 3.50 (3.44) |
| i | Cl | 2-C ₁₀ H ₇ | C ₆ H ₅ | 60 | 170-72 | 170-72 | C | 85.57 (85.60) | 4.59 (4.66) |
| j | Cl | 1-C ₁₀ H ₇ | 4-Cl.C ₆ H ₄ | 62 | 173-74 | 171-74 | A | 78.25 (78.20) | 4.07 (4.01) |

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|-----|----|--|---|----|--------|--------|---|------------------|----------------|
| k | Cl | 2-C ₁₀ H ₇ | 3-CH ₃ ·C ₆ H ₄ | 57 | 189-91 | 190-92 | B | 85.53 (85.60) | 5.08 (5.02) |
| l | Cl | 4-C ₆ H ₅ ·C ₆ H ₄ | C ₆ H ₅ | 55 | 162-64 | 160-62 | C | 86.07 (86.04) | 4.78 (4.87) |
| m | Cl | 2-C ₄ H ₃ S | 4-CH ₃ O·C ₆ H ₄ | 62 | 173-74 | 172-73 | A | 71.80 (71.90) | 4.33 (4.28) |
| 21a | Br | C ₆ H ₅ | C ₆ H ₅ | 58 | 92-93 | 94-96 | B | 73.40 (73.53) | 4.45 (4.56) |
| b | Br | C ₆ H ₅ | 4-CH ₃ ·C ₆ H ₄ | 60 | 113-15 | 112-14 | A | 73.90 (73.99) | 4.50 (4.56) |
| c | Br | C ₆ H ₅ | 4-CH ₃ O·C ₆ H ₄ | 65 | 124-26 | 126-28 | C | 70.05 (70.95) | 4.32 (4.37) |
| d | Br | C ₆ H ₅ | 4-Cl·C ₆ H ₄ | 62 | 115-16 | 114-16 | B | 67.15 (67.09) | 3.65 (3.56) |
| e | Br | C ₆ H ₅ | 3,4-O ₂ CH ₂ ·C ₆ H ₃ | 64 | 131-33 | 132-34 | A | 68.56 (68.49) | 3.80 (3.72) |
| f | Br | 4-CH ₃ C ₆ H ₄ | C ₆ H ₅ | 68 | 118-20 | 120-22 | C | 74.65 (74.59) | 3.85 (3.78) |
| g | Br | 4-CH ₃ C ₆ H ₄ | 4-CH ₃ O·C ₆ H ₄ | 54 | 98-100 | 96-98 | B | 71.40 (71.46) | 4.73 (4.71) |
| h | Br | 4-Cl·C ₆ H ₄ | 4-NO ₂ ·C ₆ H ₄ | 52 | 190-92 | 189-91 | C | 62.23 (62.27) | 2.85 (2.81) |
| i | Br | 2-C ₁₀ H ₇ | C ₆ H ₅ | 49 | 172-74 | 174-76 | A | 76.29 (76.28) | 4.14 (4.16) |

CONTD. Table II.1.

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|-----|-----------------|--|---|----|---------|--------|---|------------------|----------------|
| j | Br | 2-C ₁₀ H ₇ | 4-Cl.C ₆ H ₄ | 70 | 175-77 | 176-78 | B | 70.38 (70.35) | 3.58 (3.61) |
| k | Br | 1-C ₁₀ H ₇ | 3-CH ₃ .C ₆ H ₄ | 52 | 192-94 | 191-93 | B | 76.58 (76.60) | 4.48 (4.49) |
| l | Br | 4-C ₆ H ₅ .C ₆ H ₄ | C ₆ H ₅ | 50 | 161-63 | 162-64 | A | 77.20 (77.24) | 4.38 (4.36) |
| m | Br | 2-C ₄ H ₃ S | 4-CH ₃ O.C ₆ H ₄ | 54 | 172-74 | 174-76 | C | 55.54 (55.58) | 3.25 (3.26) |
| 22a | NO ₂ | C ₆ H ₅ | C ₆ H ₅ | 55 | 91-93 | 94 | A | 81.14 (81.20) | 4.63 (4.61) |
| b | NO ₂ | C ₆ H ₅ | 4-CH ₃ .C ₆ H ₄ | 68 | 110-112 | 112 | B | 81.91 (81.89) | 5.03 (5.01) |
| c | NO ₂ | C ₆ H ₅ | 4-CH ₃ O.C ₆ H ₄ | 62 | 132-34 | 128-30 | C | 77.58 (77.74) | 4.73 (4.78) |
| d | NO ₂ | C ₆ H ₅ | 4-Cl.C ₆ H ₄ | 70 | 111-13 | 115 | B | 73.90 (73.99) | 3.82 (3.89) |
| e | NO ₂ | C ₆ H ₅ | 3,4-O ₂ CH ₂ .C ₆ H ₃ | 65 | 132-34 | 133 | A | 74.75 (74.80) | 4.10 (4.06) |
| f | NO ₂ | 4-CH ₃ .C ₆ H ₄ | C ₆ H ₅ | 55 | 120-22 | 118-20 | B | 81.35 (81.41) | 5.04 (5.01) |
| g | NO ₂ | 4-CH ₃ .C ₆ H ₄ | 4-CH ₃ O.C ₆ H ₄ | 65 | 94-96 | 96 | A | 78.12 (78.10) | 5.16 (5.14) |

CONTD. Table II.1.

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|-----------------|--|---|----|--------|--------|---|------------------|----------------|
| h | NO ₂ | 4-Cl.C ₆ H ₄ | 4-NO ₂ .C ₆ H ₄ | 68 | 190-91 | 188 | B | 66.14 (66.00) | 3.27 (3.25) |
| i | NO ₂ | 2-C ₁₀ H ₇ | C ₆ H ₅ | 58 | 173 | 171-72 | A | 83.30 (83.20) | 4.61 (4.55) |
| j | NO ₂ | 2-C ₁₀ H ₇ | 4-Cl.C ₆ H ₄ | 72 | 176-77 | 178 | B | 76.14 (76.19) | 3.92 (3.90) |
| k | NO ₂ | 2-C ₁₀ H ₇ | 3-CH ₃ .C ₆ H ₄ | 52 | 189-91 | 192-94 | C | 82.63 (82.53) | 5.27 (5.29) |
| l | NO ₂ | 4-C ₆ H ₅ .C ₆ H ₄ | C ₆ H ₅ | 47 | 164-66 | 165 | B | 83.70 (83.79) | 4.76 (4.73) |
| m | NO ₂ | 2-C ₄ H ₃ S | 4-CH ₃ O.C ₆ H ₄ | 58 | 176-78 | 177 | C | 77.03 (79.74) | 5.04 (5.06) |

A = Benzene: Pet.Ether

B = Chloroform: Pet.ether

C = Benzene: Chloroform.

TABLE II.2. IR DATA (KBr) cm^{-1} OF NAPHTHALENES

| Compound | IR Data (KBr) cm^{-1} | | | | |
|----------|--------------------------------|--------------------|---------------------|-----------------------|----------------------------|
| | $\nu_{\text{C-H}}$ | $\nu_{\text{C=C}}$ | $\phi_{\text{C-H}}$ | $\nu_{\text{C-NO}_2}$ | $\nu_{\text{C-X(Cl, Br)}}$ |
| 20a | 3030 | 1595 | 990 | - | 780 |
| b | 3045 | 1595 | 995 | - | 775 |
| c | 3080 | 1598 | 992 | - | 785 |
| d | 3110 | 1610 | 995 | - | 780 |
| e | 3120 | 1605 | 992 | - | 782 |
| f | 3075 | 1605 | 995 | - | 788 |
| g | 3060 | 1585 | 992 | - | 782 |
| h | 3068 | 1610 | 995 | 1505, 1335 | 790 |
| i | 3075 | 1615 | 990 | - | 795 |
| j | 3090 | 1612 | 995 | - | 798 |
| k | 3070 | 1605 | 990 | - | 790 |
| l | 3095 | 1600 | 992 | - | 775 |
| m | 3100 | 1605 | 990 | - | 780 |
| 21a | 3045 | 1610 | 995 | - | 695 |
| b | 3050 | 1600 | 990 | - | 710 |
| c | 3085 | 1605 | 985 | - | 705 |
| d | 3095 | 1595 | 995 | - | 720 |
| e | 3105 | 1610 | 990 | - | 700 |
| f | 3130 | 1605 | 1005 | - | 695 |
| g | 3085 | 1615 | 995 | - | 685 |

CONTD. Table II.2.

| 1 | 2 | 3 | 4 | 5 | 6 |
|-----|------|------|------|------------|----------|
| h | 3105 | 1608 | 998 | 1505, 1340 | 695 |
| i | 3085 | 1600 | 990 | - | 780, 690 |
| j | 3065 | 1595 | 995 | - | 695 |
| k | 3095 | 1610 | 1000 | - | 700 |
| l | 3075 | 1605 | 998 | - | 675 |
| m | 3110 | 1610 | 995 | - | 695 |
| 22a | 3095 | 1605 | 992 | 1500, 1330 | - |
| b | 3090 | 1608 | 998 | 1515, 1335 | - |
| c | 3100 | 1615 | 990 | 1520, 1325 | - |
| d | 3070 | 1605 | 992 | 1510, 1320 | - |
| e | 3090 | 1595 | 990 | 1505, 1310 | - |
| f | 3105 | 1605 | 995 | 1505, 1345 | - |
| g | 3122 | 1605 | 992 | 1500, 1340 | - |
| h | 3145 | 1618 | 988 | 1510, 1325 | - |
| i | 3110 | 1605 | 996 | 1515, 1335 | - |
| j | 3105 | 1610 | 992 | 1525, 1335 | - |
| k | 3115 | 1600 | 982 | 1505, 1310 | - |
| l | 3060 | 1598 | 990 | 1500, 1325 | - |
| m | | | | | |

ν = Stretching vibrations

ϕ = Out of the plane deformations
of hydrogen attached to aromatic
nucleus.

TABLE II.3. NMR (CDCl_3) DATA OF NAPHTHALENE DERIVATIVES (20a-22m).

| Compound | δ (ppm) | No.of protons | Assignment of protons |
|----------|----------------|---------------|--------------------------|
| 1 | 2 | 3 | 4 |
| 20a | - | - | - |
| b | 2.50, s | 3H | CH_3 |
| | 6.92-8.22, m | 14H | Phenyl+naphthyl |
| c | 3.80, s | 3H | OCH_3 |
| | 6.82-8.24, m | 14H | Phenyl+naphthyl |
| d | - | - | - |
| e | 6.05, s | 2H | $-\text{O}_2\text{CH}_2$ |
| | 6.72-8.15, m | 13H | Phenyl+naphthyl |
| f | 2.45, s | 3H | CH_3 |
| | 6.80-8.15, m | 14H | Phenyl+naphthyl |
| g | 3.75, s | 3H | OCH_3 |
| | 2.35, s | 3H | CH_3 |
| | 6.85-8.26, m | 13H | Phenyl+naphthyl |
| i | - | - | - |
| j | - | - | - |
| k | 2.35, s | 3H | CH_3 |
| | 6.80-8.25, m | 16H | Phenyl+naphthyl |
| m | 3.80, s | 3H | OCH_3 |
| | 6.88-8.20, m | 12H | Phenyl+naphthyl |

CONTD. Table II.3.

| 1 | 2 | 3 | 4 |
|-----|--------------|-----|--------------------------------|
| 21a | - | - | - |
| b | 2.40, s | 3H | CH ₃ |
| | 6.85-8.25, m | 14H | Phenyl+naphthyl |
| c | 3.75, s | 3H | OCH ₃ |
| | 6.75-8.20, m | 14H | Phenyl+naphthyl |
| d | - | - | - |
| e | 6.00, s | 2H | O ₂ CH ₂ |
| | 6.65-8.10, m | 13H | Phenyl+naphthyl |
| f | 2.40, s | 3H | CH ₃ |
| | 6.75-8.10, m | 14H | Phenyl+naphthyl |
| g | 3.70, s | 3H | OCH ₃ |
| | 2.30, s | 3H | CH ₃ |
| | 6.80-8.20, m | 13H | Phenyl+naphthyl |
| h | - | - | - |
| i | - | - | - |
| j | - | - | - |
| k | 2.45, s | 3H | CH ₃ |
| | 6.80-8.20, m | 16H | Phenyl+naphthyl |
| l | - | - | - |
| m | 3.70, s | 3H | OCH ₃ |
| | 6.65-8.10, m | 12H | Phenyl+naphthyl |

CONTD. Table II.3.

| 1 | 2 | 3 | 4 |
|-----|--------------|-----|-----------------------------------|
| 22a | - | - | - |
| b | 2.48, s | 3H | CH ₃ |
| | 6.95-8.30, m | 14H | Phenyl+naphthyl |
| c | 3.87, s | 3H | OCH ₃ |
| | 6.87-8.29, m | 14H | Phenyl+naphthyl |
| d | - | - | - |
| e | 6.03, s | 2H | -O ₂ CH ₂ - |
| | 6.72-8.15, m | 13H | Phenyl+naphthyl |
| f | 2.33, s | 3H | CH ₃ |
| | 6.77-8.18, m | 14H | Phenyl+naphthyl |
| g | 2.35, s | 3H | CH ₃ |
| | 3.75, s | 3H | OCH ₃ |
| | 6.80-8.21, m | 13H | Phenyl+naphthyl |
| h | - | - | - |
| i | - | - | - |
| j | - | - | - |
| k | 2.36, s | 3H | CH ₃ |
| | 6.82-8.30, m | 16H | Phenyl+naphthyl |
| l | - | - | - |
| m | 3.82, s | 3H | OCH ₃ |
| | 6.84-8.26, m | 12H | Phenyl+naphthyl +thiophenyl |

s = singlet

m = multiplet

CHAPTER III

CHAPTER-III

SYNTHESIS OF SOME NEW 2,4,6-TRIARYL SUBSTITUTED PYRIDINES:
USING STABILIZED π -SULFURANES : REACTION OF 4-METHOXY
PHENACYLDIMETHYL SULFONIUM YLIDE WITH α, β -UNSATURATED
KETONES:

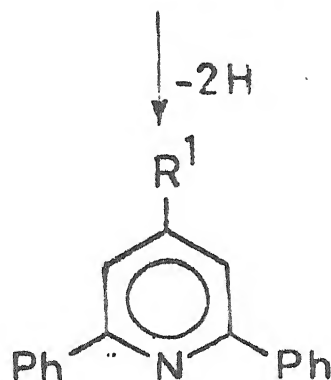
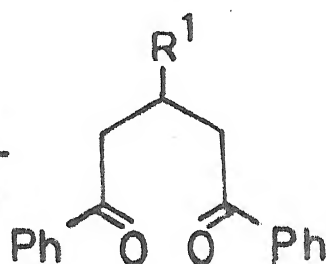
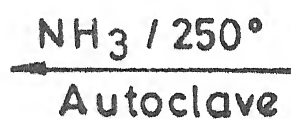
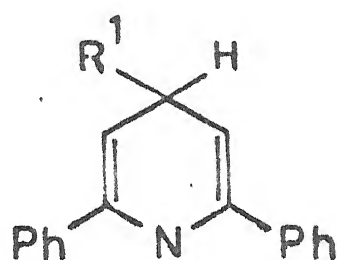
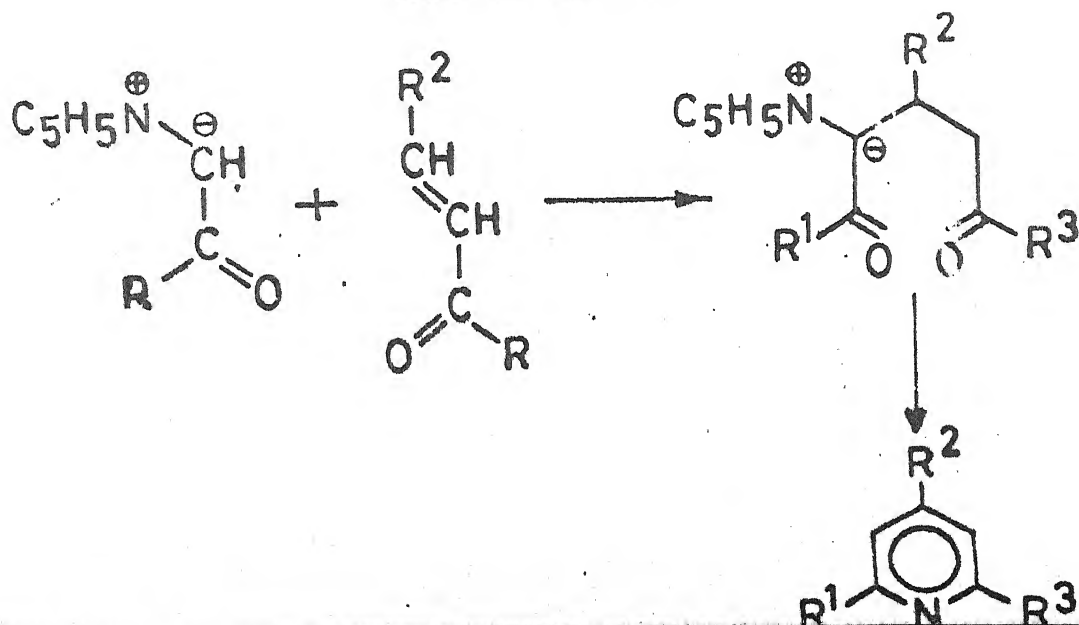
III.1. ABSTRACT :

A 4-methoxyphenacyldimethyl sulfonium bromide was prepared by heating 4-methoxyphenacyl bromide and dimethyl sulfide in benzene or acetone at reflux temperature. The sulfonium salt on treatment with aq. NaOH in methanolic solution gave 4-methoxyphenacylidene dimethyl sulfurane. The salt or ylide on reaction with α, β -unsaturated ketones in presence of ammonium acetate in acetic acid or methanol gave asymmetrical pyridines having different substituents at 2,4,6-positions. Similarly, when the salt or ylide was reacted with 4-methoxyacetophenones in presence of ammonium acetate, 2,6-di(4-methoxyphenyl)4-arylpyridines having identical substituents at C_2 and C_6 position was formed. Attempts to synthesize symmetrical pyridines having identical substituents at 2,4,6 position involved the condensation of salt or ylide with 4-methoxy benzal-4-methoxyacetophenone in ammonium acetate in acetic acid. All pyridines were confirmed by IR and NMR spectral data.

III.2. INTRODUCTION :

On the earlier methods involving aza ring closure leading to the synthesis of substituted pyridines was first reported by Tschitschibabin¹. The method involved the condensation of aldehyde and methyl ketone in presence of liquid ammonia (Scheme III.1). But this method was not versatile because of harsh reaction conditions and poor yields of products. Subsequent to this report, Frank et al^{2,3} made an improvement over the earlier reported method by using ammonia and catalytic amount of ammonium acetate.

Later on Krohnke et al^{4,5} developed a superior method, involving the interaction of pyridinium salts or ylides with α, β -unsaturated ketones (Scheme III.2). The course of the reaction involves the same penta-1,5-dionyl intermediate, analogous to the diketone intermediate formed in earlier methods. The intermediate undergoes aza ring closure with ammonium acetate in glacial acetic acid to give 2,4,6-triaryl pyridines. The superiority of Krohnke's method^{4,5} over Tschitschibabin's method¹ lies in the requirement of mild reaction conditions and better yields of pyridines. Moreover, earlier methods^{1,3} were restricted to the preparation of symmetrical pyridine having identical substituents at 2 & 6 positions of pyridine ring. The Krohnke's^{4,5} method allows the synthesis of both symmetrical and asymmetrical pyridine

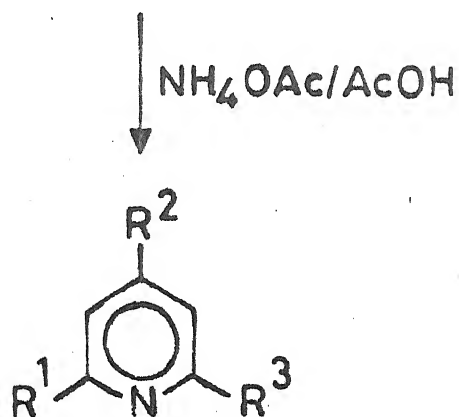
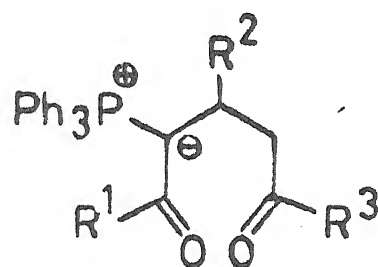
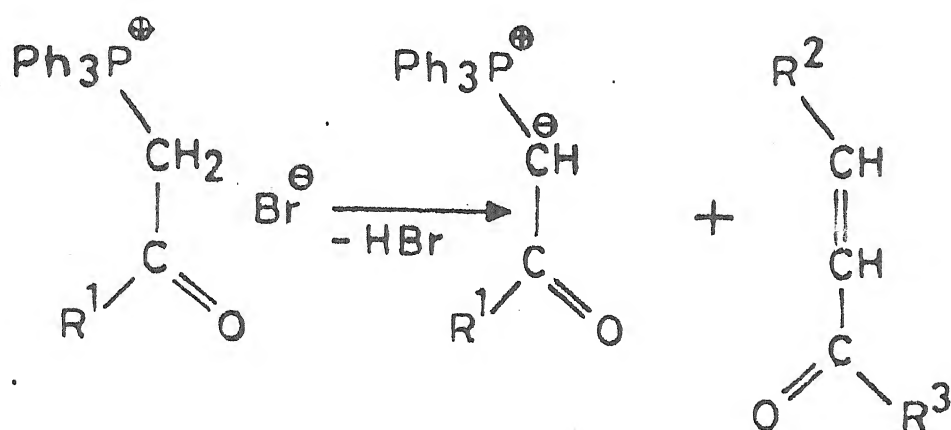
Scheme III-1Scheme III-2

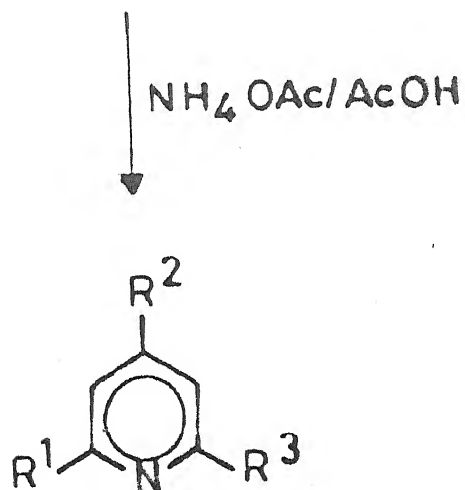
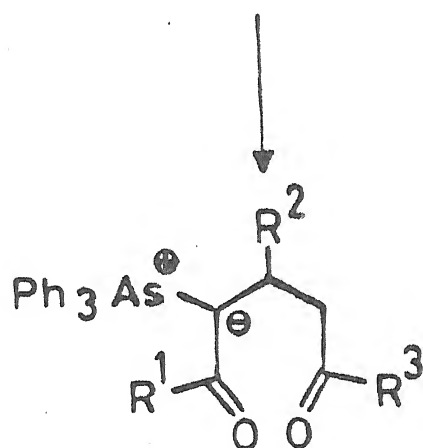
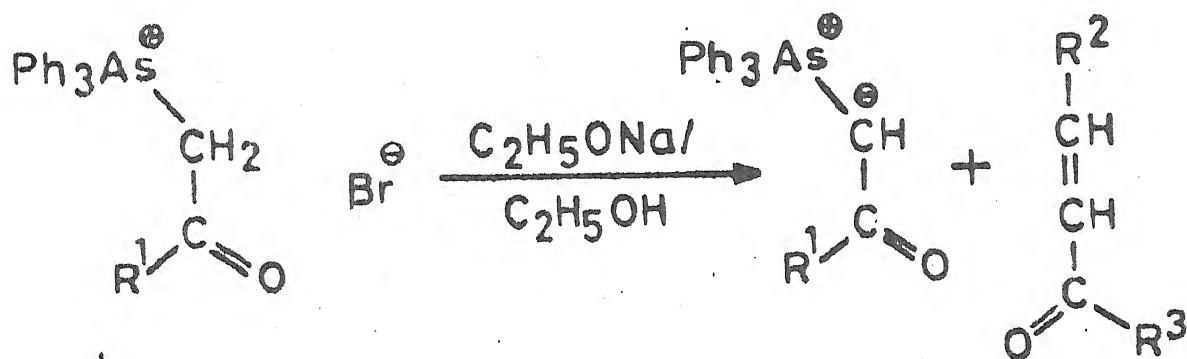
having different substituents at 2,4,6-positions of pyridines nucleus.

After the report of Krohnke^{4,5}, several pioneer workers reported⁶⁻⁹ the synthesis of new 2,4,6-triaryl pyridines using phenacyl pyridinium ylides or salts with a view to test the domain of the applicability of the reaction.

Recently phosphonium¹⁰ (Scheme III.3) and Arsonium¹¹ (Scheme III.4) ylides are also reported to couple with α, β - unsaturated ketones in presence of ammonium acetate leading to the synthesis of pyridine nucleus analogous to the corresponding pyridinium ylide and follows the similar course of reaction as reported for pyridinium ylide. But these routes¹⁰ for the preparation of pyridine nucleus were not much facile as it involved the separation of leaving group triphenylphosphine or triphenyl arsine from the reaction mixture whereas in the former method^{4,9} leaving group was washed out.

Literature reveals that sulfonium ylides and their precursors have been used in the synthesis of a large variety of cyclic and heterocyclic systems viz. cyclopropanes^{12,13}, epoxides¹⁴, indoles^{15,16}, aziridines¹⁷ and tetrazines¹⁸. Tewari et al¹⁹ in a few reactions reported that sulfonium salt or ylide also underwent aza ring closure reaction leading to the synthesis of pyridine nucleus. But the domain of the applicability of this reaction could not be duplicated

SCHEME III-3

SCHEME III.4

until recently.

Therefore, it seemed to be pertinent to elaborate some more reactions of sulfonium salts and their π -sulfuranes with a view to test the domain of synthetic applicability. In the present chapter, we have reported the synthesis of some asymmetrical and symmetrical methoxypyridines having various different substituents by the condensation of p-methoxy phenacylidinedimethyl sulfurane with a wide variety of α, β -unsaturated ketones in presence of ammonium acetate in acetic acid.

III.3. RESULTS AND DISCUSSION :

Condensation of 4-methoxyphenacyl bromide prepared by the bromination of 4-methoxy acetophenone with DMS gave 4-methoxyphenacyldimethyl sulfonium bromide(1). The structure of salt (1) was evidenced by IR and NMR spectral data. The IR spectrum of salt (1) displayed a strong band at 1675 cm^{-1} due to $\text{C}=\text{O}$. The NMR spectrum showed a strong singlet at $\delta 3.05$ due to two methyl groups directly linked to sulfonium group. A sharp singlet at $\delta 5.35$ revealed the methylene protons adjacent to the sulfonium group. The methoxy group appeared at $\delta 3.75$ and aromatic protons were observed in the range $\delta 7.15-7.80$.

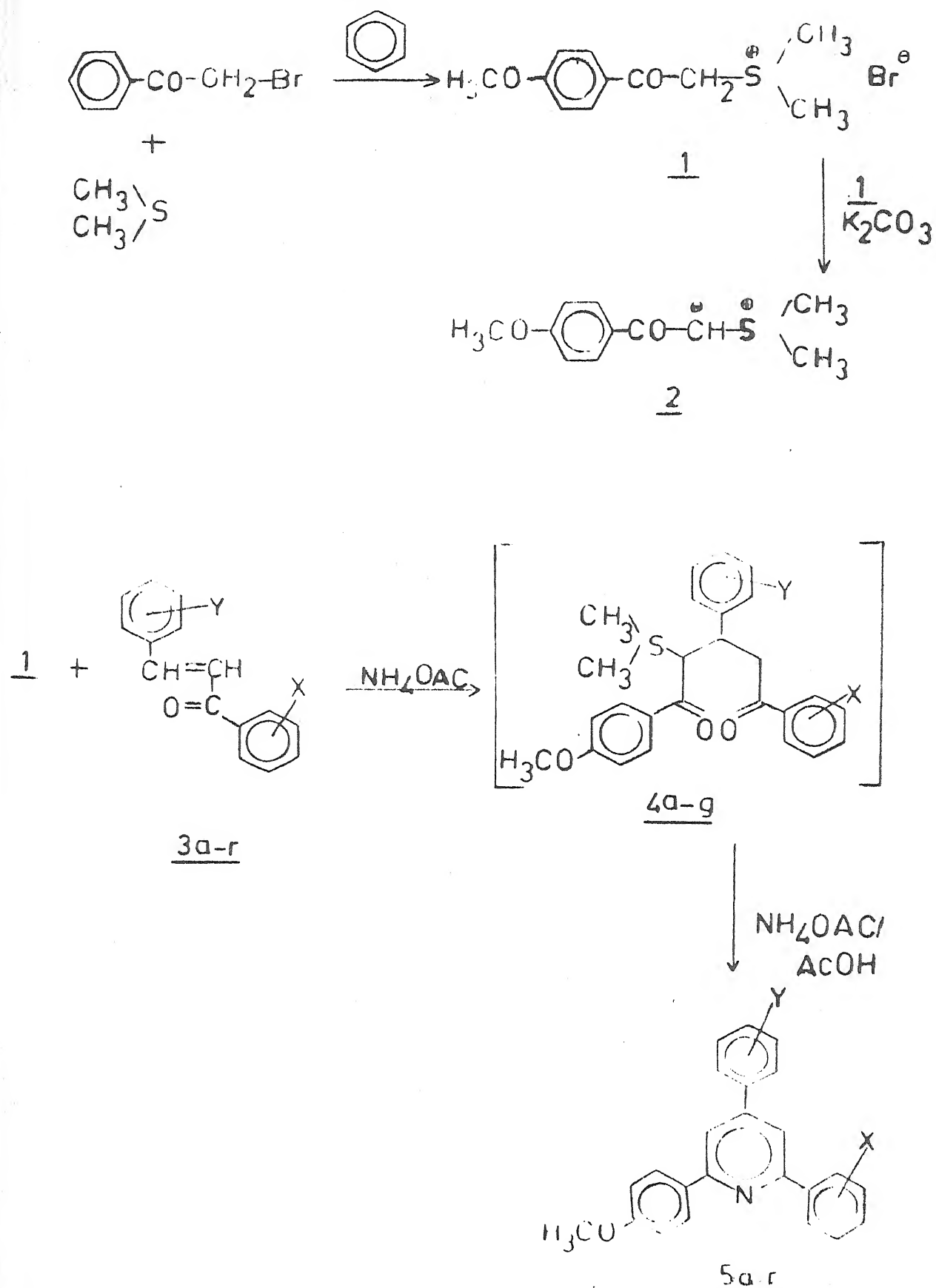
Salt (1) on treatment with aq.NaOH generated a yellow colouration which was changed into orange colour clearly

indicating the formation of ylide 4-methoxyphenacyldimethyl sulfurane (2). The (2) was isolated in the form of yellowish orange crystals owing to resonance stabilizing factors. The structures of ylide (2) was confirmed on the basis of IR and NMR spectral data. The IR spectrum showed a band of medium intensity in the region 1520 cm^{-1} due to C=O stretching vibrations. This absorption is diagnostic of enolate structure. The NMR spectrum showed a singlet at $\delta 3.15$ due to two methyl protons. A methine proton adjacent to sulfonium group was observed at $\delta 4.20$. The aromatic multiplet was observed in the region $\delta 7.20-8.15$.

Ylide (2) so generated was though isolable but could not be stored for quite long time owing to its susceptibility towards atmospheric components and therefore, it was difficult to use ylide as starting material in the pyridine synthesis. Therefore salt (1) was used in the reaction and ylide (2) was generated in situ from its salt(1). Heating the mixture of salt (1) with α, β -unsaturated ketones (3a-r) in presence of ammonium acetate and glacial acetic acid gave 2,4,6-triarylpyridines (5a-r) in 45-70% yields(Scheme III.5).

Similarly, symmetrical pyridines 2,6-di(4-methoxyphenyl)-4-arylpyridines (5f-i) were also synthesized in 40-70% yields by the reaction of salt with substituted benzylidene-4-methoxy acetophenones (3f-i) in a mixture of ammonium acetate and acetic acid(Scheme III.6).

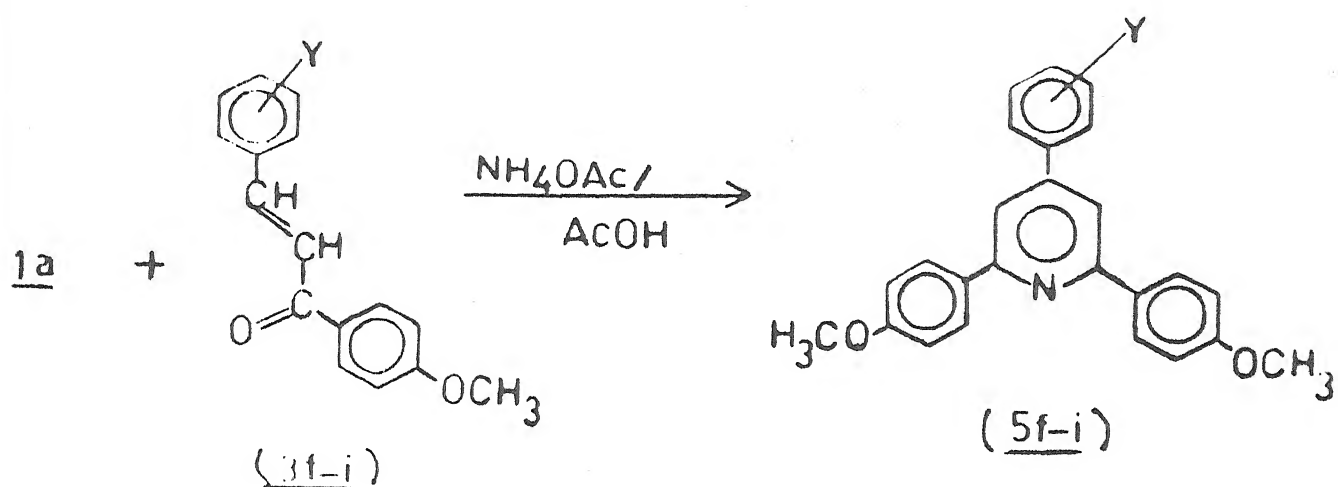
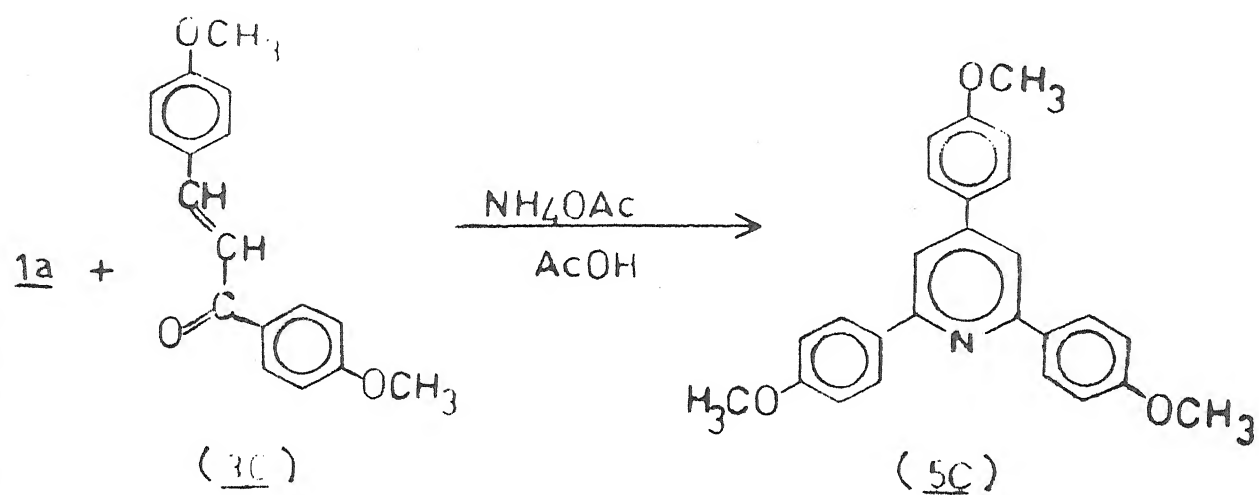
Scheme III.5



Next attention was towards the synthesis of pyridine (5c) having identical substituents at 2,4,6-positions of pyridine nucleus. This was achieved by heating salt (1) with 4-methoxybenzylidene-4-methoxy acetophenone (31) in presence of ammonium acetate in acetic acid giving 50% yield (Scheme III.7).

The course of reaction seems to be proceeded by the attack of ylide carbanion (2) on β -carbon of α, β -unsaturated ketones (3) to form pentane-1,5-dionyl dimethyl sulfonium ylide intermediates (4a-r) which, in turn, undergo aza ring closure in presence of ammonium acetate to form 2,4,6-triarylpyridines (5a-r).

Various methoxypyridines (5a-r) prepared by the above method are listed in table III.1. All the pyridines gave satisfactory elemental analysis the melting point of the pyridines obtained by route abovesaid were very closed to that reported in literature²⁰. The structures of pyridines were confirmed by spectral data²¹. The IR spectral data showed characteristic absorption bands in the region $3050-3000\text{cm}^{-1}$, which were assigned to the C-H stretching mode of pyridine rings. Two bands the region 1600 and 1500cm^{-1} were due to the interaction between C=C and C=N vibrations of the pyridine rings. The NMR spectrum of the pyridines showed two pyridyl protons in the range $\delta 6.35-6.65$ and aromatic protons in the region $\delta 6.40-8.05$.

Scheme III. 6Scheme. III. 7

III.4. EXPERIMENTAL :

Starting Material :

All the reagents obtained sources (E. Merck, B.D.H., SISCO, Polyform Fluka) starting materials were prepared according to the procedures reported in literature. 4-methoxyphenacyl bromide was prepared by the bromination of 4-methoxyacetophenone in either-dioxan method²². The benzylidene acetophenone were prepared by the condensation of substituted acetophenones with substituted benzaldehydes dissolved in alcoholic solution containing NaOH²³.

III.4.1. Preparation of 4-methoxyphenacyl dimethyl sulfonium bromide (1) :

Stirring a mixture of 4-methoxyphenacyl bromide (0.1 mole) and dimethyl sulfide (30ml) for 8 hrs gave white solid mass. The solid mass was filtered, washed twice with ether and recrystallized from alcohol as white colourless microcrystals m.p. 122-124°C (Lit.²⁰ 118-120°C).

IR Data (KBr) : 1675cm^{-1} ($\nu_{\text{C=O}}$)

NMR (CDCl_3) Data (δ ppm) : 3.05(s, 6H, di CH_3) : 3.75(s, 3H, OCH_3) :

5.10(s, 2H, $\text{CH}_2\text{-S}^+$) : 7.08-8.22(m, 4H, ArH)

III.4.2. Preparation of 4-methoxyphenacylidine dimethyl sulfurane (2) :

4-Methoxyphenacyldimethylsulfonium bromide (1) (50m mole) was dissolved in water (30ml). The coloured suspension

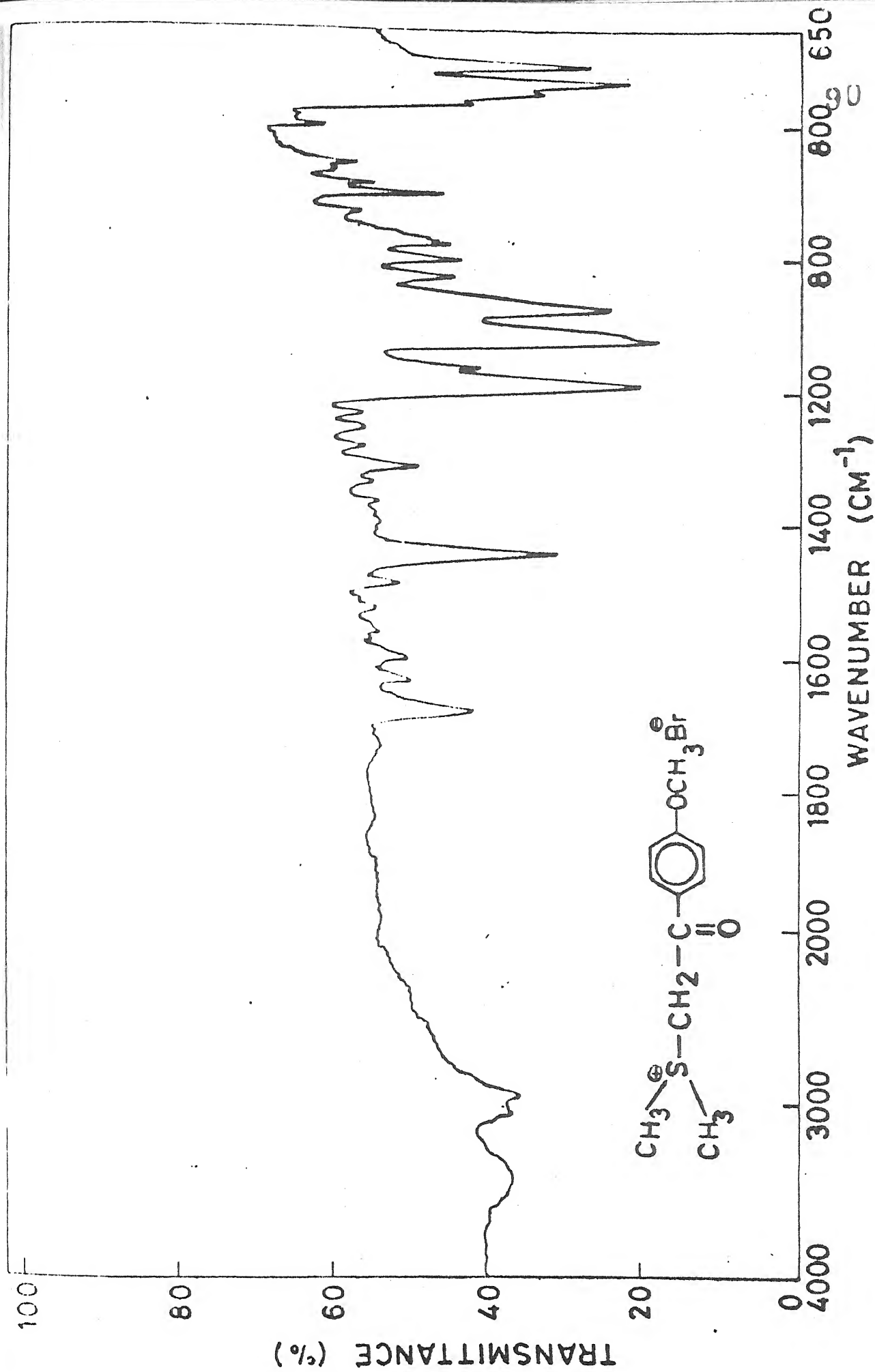
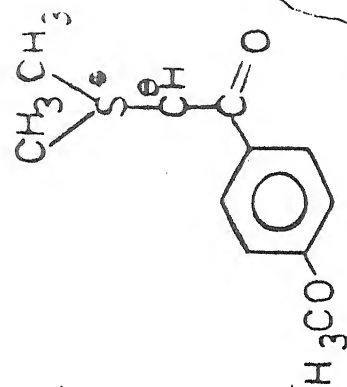


FIG. III-1 IR SPECTRUM OF SALT (1)



Transmittance (%)

91

Frequency (cm^{-1})

FIGIII.2 IR SPECTRUM OF 2...

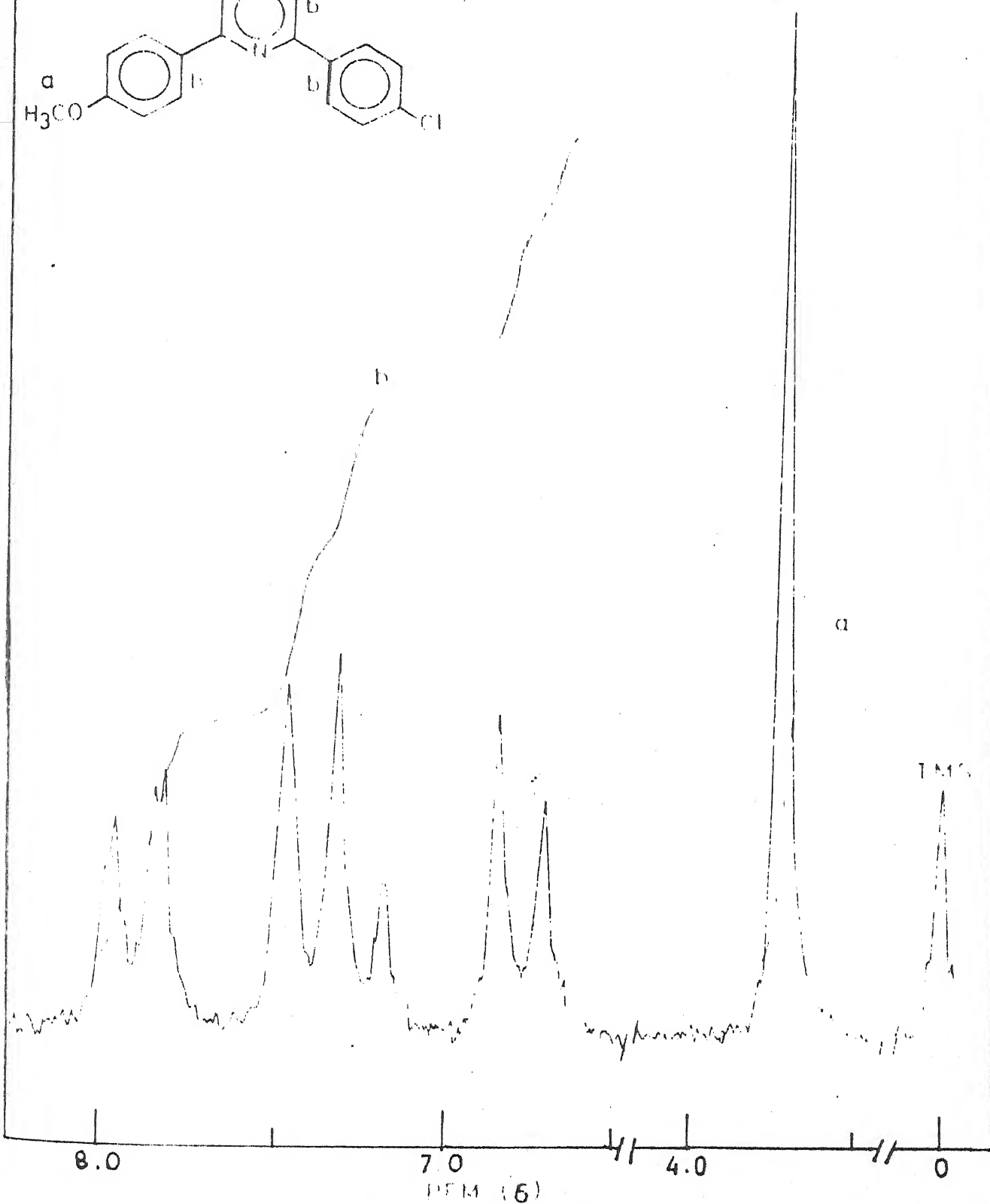
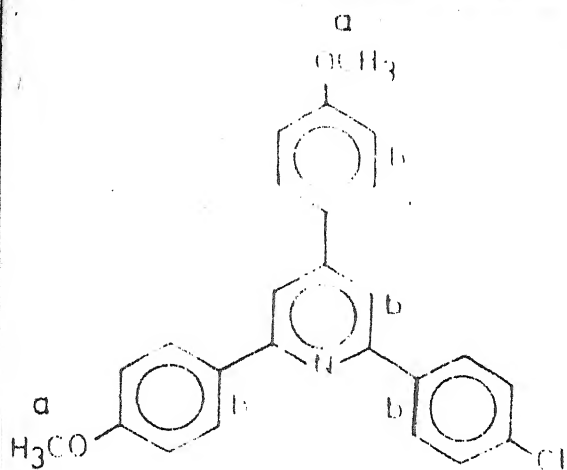


FIG. III.3 NMR SPECTRUM OF **5a**

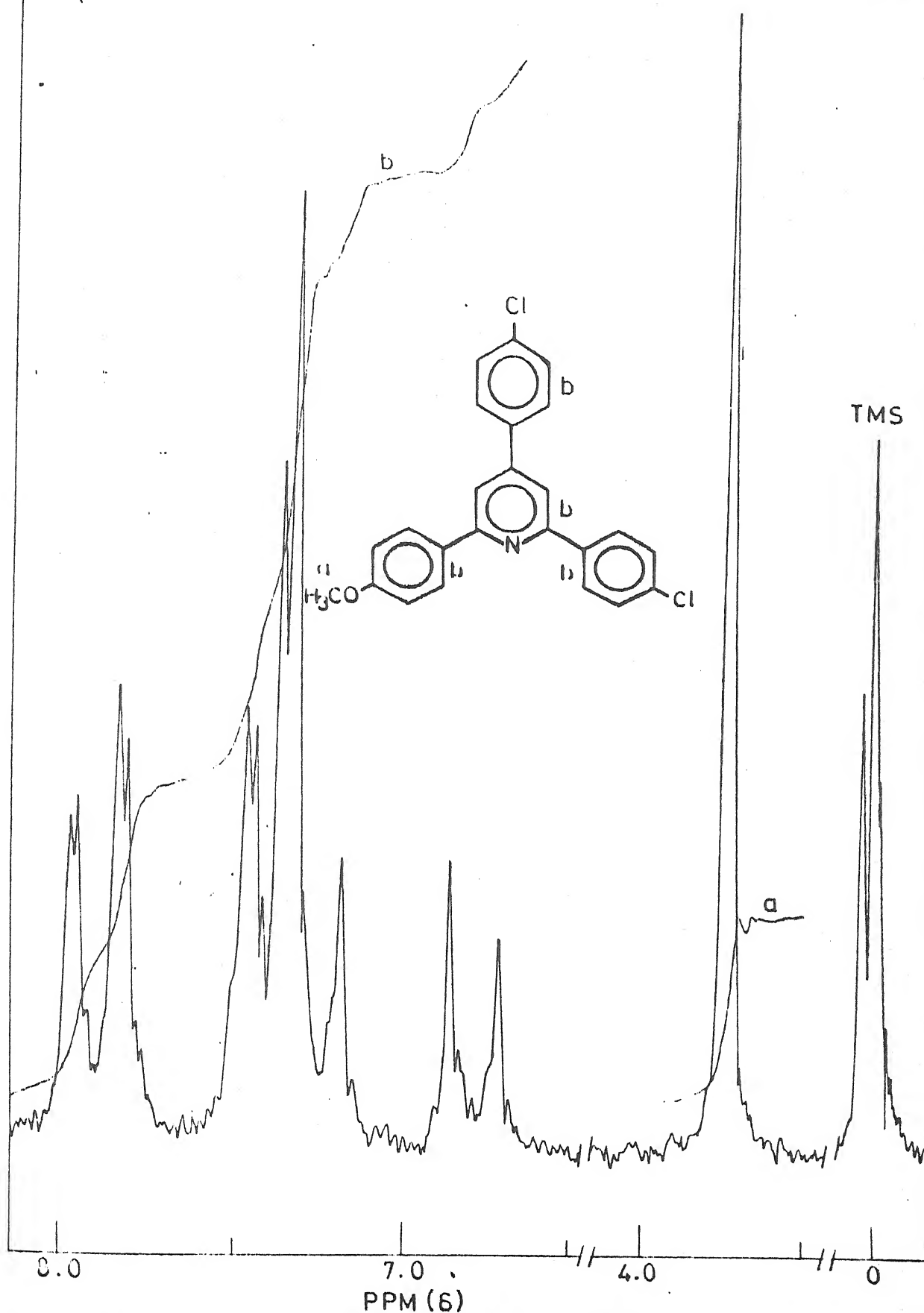
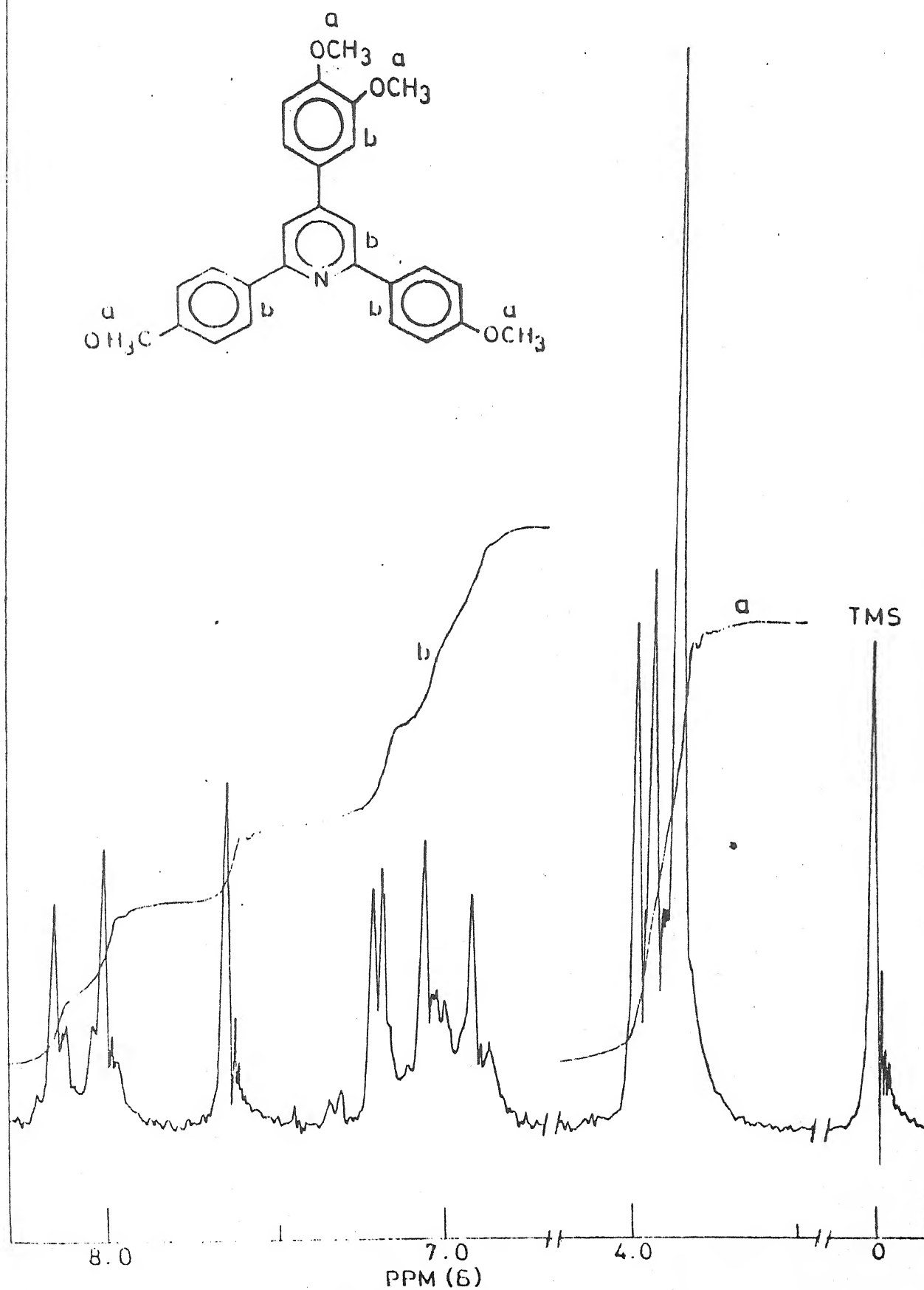


FIG. III.4 NMR SPECTRUM OF **5b**.

FIG. III. 5 NMR SPECTRUM OF 5h.

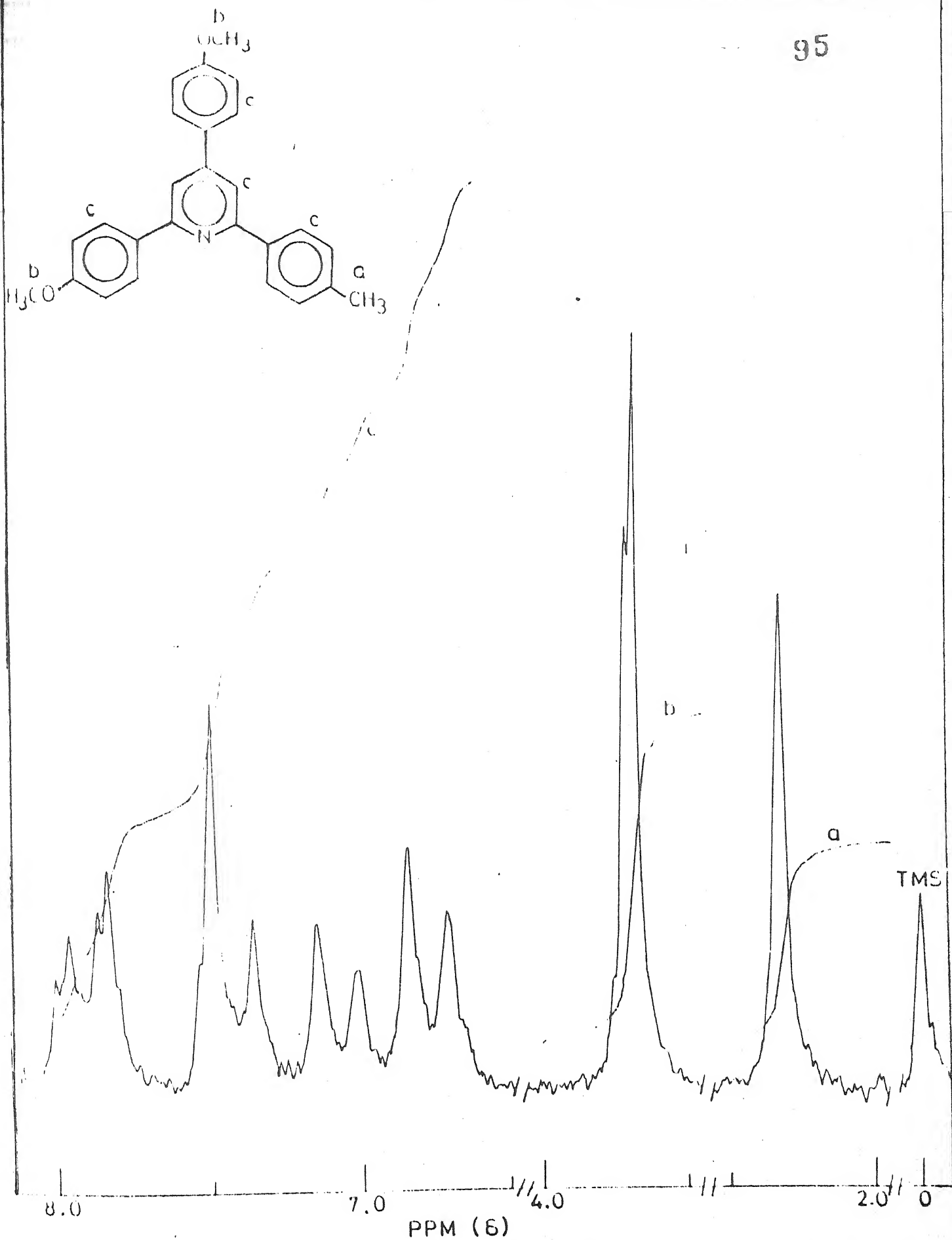


FIG. III.6 NMR SPECTRUM OF 51.

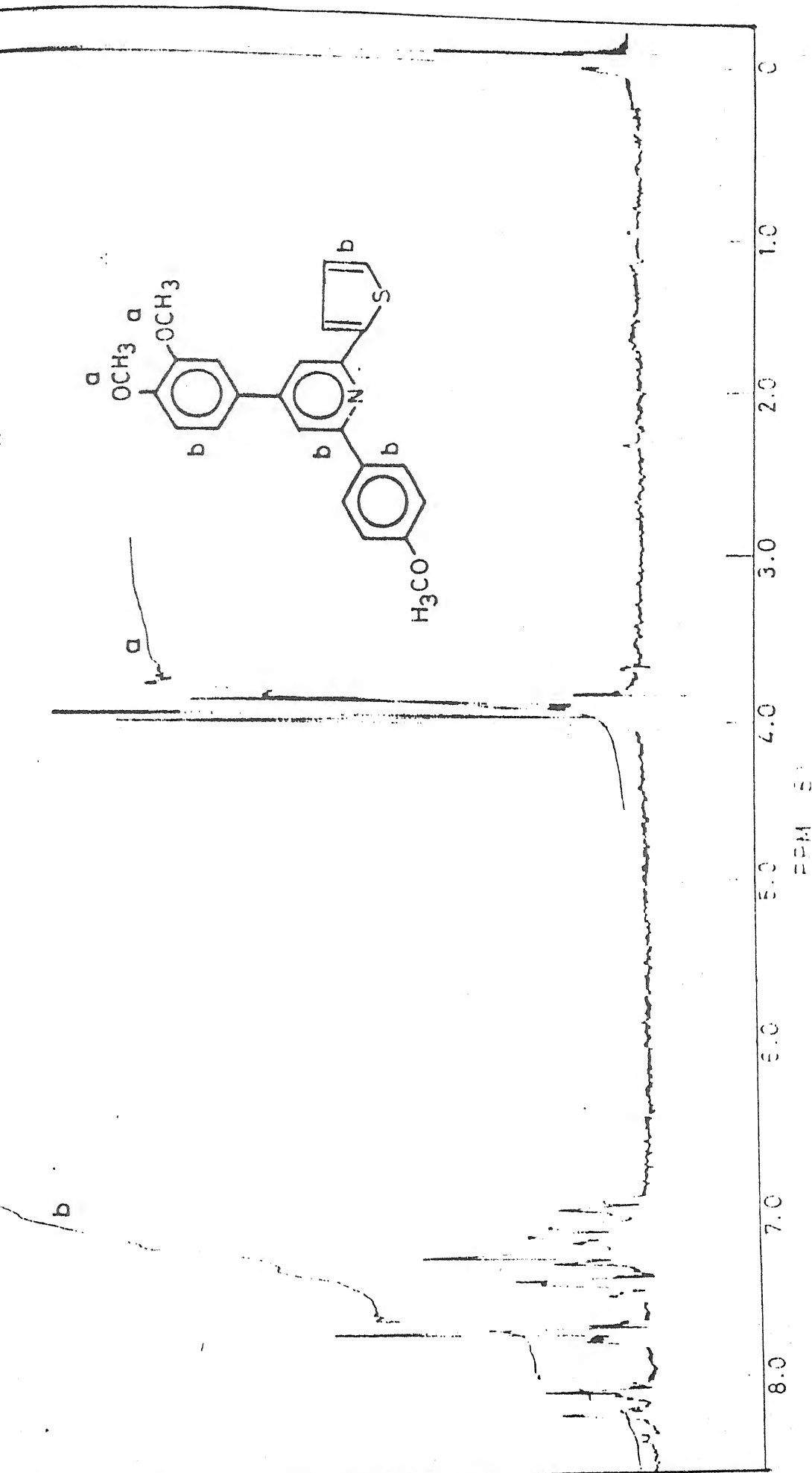


FIG. III. 7 NMR SPECTRUM OF SO

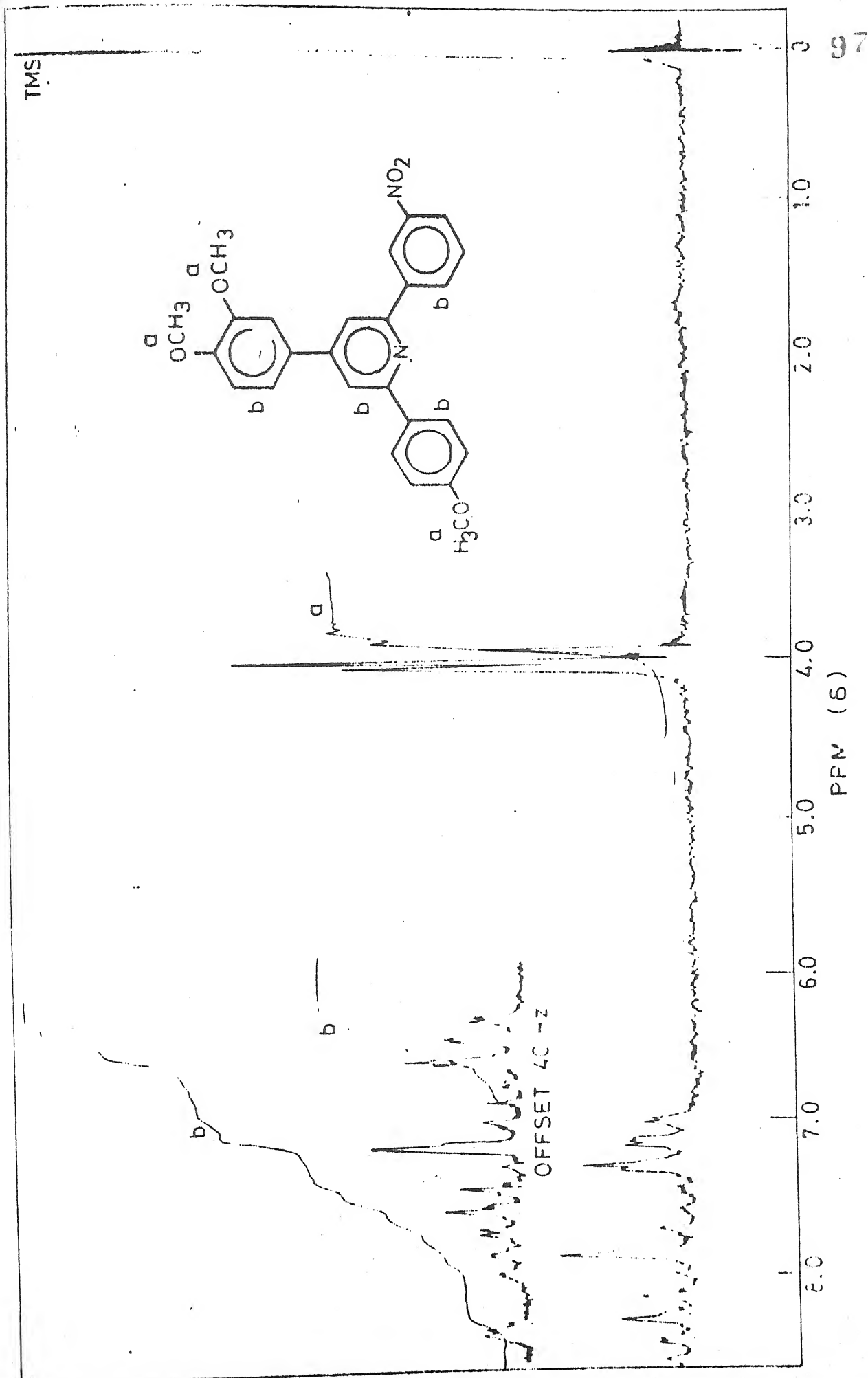


FIG. 11.8 NMR SPECTRUM OF 5f.

was filtered and the clear filtrate was treated with 10% aq. NaOH (15ml). The solution was stirred for 8 hrs, and then extracted several times with CHCl_3 . The chloroform extract was dried with sodium sulphate and evaporated to give yellow oil which on cooling gave yellow solid. The yellow solid on crystallization with ethanol afforded reddish yellow crystals of 4-methoxyphenacylidenedimethyl sulfurane (2) in 80% yields which melted at $86-88^\circ\text{C}$ (Lit.²⁰ m.p. 90°C).

IR Data (KBr) : $1500-1520\text{Cm}^{-1}$

NMR(CDCl_3) data(δ ppm) : 3.15(s, 6H, di CH_3) : 3.70(s, 3H, OCH_3) :
4.20(s, 1H, $\bar{\text{C}}\text{H}-\text{S}^+$) : 7.20-8.15(m, 4H, Ar-H) .

III.4.3. General Procedure for preparation of 2,4,6-triarylpyridines (5a-r) :

To a stirred mixture of 4-methoxyphenacyl sulfonium bromide (1) (3m mole) and ammonium acetate (3g) in glacial acetic acid (25ml), a solution of disubstituted benzylidene acetophenone (3a-r) (3m mole) dissolved in 20ml of glacial acetic acid was added dropwise by dropping funnel at the reflux temperature in an atmosphere of nitrogen. After complete addition of chalcone, the mixture was refluxed for 3-6 hrs and then left overnight at the room temperature. The mixture was then poured in ice cold water (50ml) which was constantly stirred. The solid mass precipitated, filtered and then washed with methanol. The product, on crystallization with an appropriate solvent, gave crystalline titled pyridines(5a-r) in 40-80% yields as depicted in table III.1.

REFERENCES

1. A.B. Tschitschibabin, Bull.Soc.Chem., 4, 1826 (1937); J. Russ.Chem.Soc., 37, 1229 (1905); J.Prakt.Chem., 107, 122 (1924).
2. R.L. Frank and R.P. Seven, J.Am.Chem.Soc., 71, 2629 (1949).
3. R.L. Frank and E.F. Piever, J.Am.Chem.Soc., 72, 4182 (1950).
4. F. Krohnke and W. Zecher, Angew Chem.Int.Ed., 1, 626 (1962); Angew.Chem., 94, 690 (1961); 95, 1128 (1962).
5. F. Krohnke, Synthesis, 1, (1976)
6. R.S. Tewari and K.C. Gupta, Indian J.Chem., 13, 864 (1975).
7. R.S. Tewari, K.C. Gupta and A.K. Dube, Indian J.Chem., 20B, 706 (1981); J.Ind.Chem.Soc., L11, 1035 (1980).
8. K.C. Gupta, N. Srivastava, R.K. Nigam and S. Malik, Indian J.Chem., 21B, 242 (1982).
9. S. Malik, K. Pandey, B. Raj and K.C. Gupta, J.Chem. Engg.Data, 28, 430 (1983).
10. K.C. Gupta, N. Srivastava and R.K. Nigam, Curr.Sci., 52, 719 (1983).
11. K.C. Gupta, N. Srivastava and R.K. Nigam, J.Organomet. Chem., 204, 55 (1981).

12. R.S. Tewari and A.K. Awasthi, Indian J.Chem., 19B, 155 (1980).
13. R.S. Tewari and D.K. Nagpal, J.Ind.Chem.Soc., LVI, 911 (1979).
14. J.D. Ballantine and P.J. Sykes, J.Chem.Soc., 731(1970).
15. R.K. Bansal and S.K. Sharma, Tetrahydron Letters, 1923 (1977); J.Organomet.Chem., 149, 309 (1978).
16. H. Junjappa, Synthesis, 798 (1975).
17. R.S. Tewari, A.K. Awasthi and Anita Awasthi, Synthesis 330 (1983).
18. R.S. Tewari, A.K. Awasthi and P. Parihar, Synthesis, 334 (1983).
19. R.S. Tewari and A.K. Awasthi, Synthesis, 314 (1981).
20. R.S. Tewari and N.K. Mishra, J.Heterocycl.Chem., 17, 953 (1980).
21. L.J. Bellamy, "The Infrared Spectra of Complex Molecules", Wiley, New York, pp 271-81 (1954).
22. B.M. Trost, J.Am.Chem.Soc., 89, 138 (1962).
23. H. Gilmann and A.H. Blatt, "Organic Synthesis", John Wiley and Sons, New York, Coll.Vol.1, pp 78 (1958).

TABLE III.1. PHYSICAL PROPERTIES OF 2,4,6-TRIARYLPYRIDINES (5a-r)

| Comp- ound | X | Y | Yield % | M.P. °C | Lit. M.P. °C | Recry- stn. Solve- nt | Anal. data found/(Calcd.) | | |
|---------------|--------------------|--------------------------------------|------------|------------|--------------------|--------------------------------|---------------------------|----------------|----------------|
| | | | | | | | C% | H% | N% |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| 5a | 4-Cl | 4-OCH ₃ | 64 | 143 | 144-45 | A | 74.69 (74.71) | 4.95 (4.98) | 3.46 (3.48) |
| b | 4-Cl | 4-Cl | 72 | 196 | 195 | A | 70.91 (70.93) | 4.20 (4.18) | 3.45 (3.44) |
| c | 4-OCH ₃ | 4-OCH ₃ | 56 | 124 | 126-27 | A | 78.55 (78.55) | 5.77 (5.79) | 3.54 (3.52) |
| d | 4-Cl | 4-N(CH ₃) ₂ | 62 | 127-29 | 128-30 | A | 75.28 (75.27) | 5.56 (5.54) | 6.72 (6.75) |
| e | 4-Cl | 3,4-(OCH ₃) ₂ | 59 | 119-21 | 118-20 | A | 72.32 (72.30) | 5.06 (5.09) | 3.21 (3.24) |
| f | 4-OCH ₃ | 4-Cl | 76 | 124-28 | 125-30 | A | 74.70 (74.71) | 4.96 (4.98) | 3.46 (3.48) |
| g | 4-OCH ₃ | 4-N(CH ₃) ₂ | 73 | 111-13 | 110-12 | B | 79.00 (79.02) | 6.36 (6.34) | 6.80 (6.82) |
| h | 4-OCH ₃ | 3,4-(OCH ₃) ₂ | 52 | 81-83 | 80-82 | B | 75.84 (75.87) | 5.86 (5.85) | 3.28 (3.27) |
| i | 4-OCH ₃ | 3,4-CH ₂ O ₂ | 59 | 124-26 | 125-26 | B | 75.89 (75.91) | 5.08 (5.10) | 3.38 (3.40) |

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|-----------------------------------|--------------------------------------|----|--------|--------|---|------------------|----------------|----------------|
| j | 4-Cl | 3,4-CH ₂ O ₂ | 53 | 134-39 | 135-40 | B | 72.16 (72.20) | 4.31 (4.33) | 3.38 (3.36) |
| k | 4-CH ₃ | 3,4-CH ₂ O ₂ | 82 | 86 | 85 | C | 72.95 (72.98) | 5.30 (5.31) | 3.52 (3.54) |
| l | 4-CH ₃ | 4-OCH ₃ | 61 | 103-5 | 104-5 | B | 81.86 (81.88) | 6.04 (6.03) | 3.65 (3.67) |
| m | 2-C ₁₀ H ₇ | C ₆ H ₅ | 66 | 194 | 195 | B | 86.89 (86.91) | 6.04 (6.07) | 3.25 (3.27) |
| n | 2-C ₁₀ H ₇ | 4-CH ₃ | 47 | 133-34 | 135-36 | B | 86.84 (86.87) | 6.31 (6.33) | 3.14 (3.16) |
| o | 2-C ₄ H ₃ S | 3,4-(OCH ₃) ₂ | 53 | 96-98 | 97-98 | B | 71.43 (71.46) | 5.19 (5.21) | 3.49 (3.47) |
| p | 4-CH ₃ | 3,4-(OCH ₃) ₂ | 63 | 110-16 | 112-15 | B | 72.84 (72.83) | 6.07 (6.08) | 3.40 (3.40) |
| q | 4-C ₆ H ₅ | C ₆ H ₅ | 71 | 97 | 98 | B | 86.72 (86.74) | 6.01 (6.02) | 3.35 (3.37) |
| r | 3-NO ₂ | 3,4-(OCH ₃) ₂ | 62 | 144-47 | 146-47 | C | 70.55 (70.58) | 4.96 (4.97) | 6.36 (6.37) |

A = Chloroform; ethanol B = Pyridine methanol C = Pyridine methanol water.

TABLE III.2. IR DATA (KBr) cm^{-1} 2,4,6-TRIARYLPYRIDINES (5a-r)

| Compound | IR Data (KBr) cm^{-1} | | | |
|----------|--------------------------------|------------------|------------------|-------------------|
| | $\nu \text{C-H}$ | $\nu \text{C=C}$ | $\nu \text{C=N}$ | $\phi \text{C-H}$ |
| 5a | 3030 | 1600 | 1550 | 995 |
| b | 3040 | 1605 | 1545 | 998 |
| c | 3030 | 1610 | 1552 | 990 |
| d | 3020 | 1595 | 1530 | 1005 |
| e | 2948 | 1598 | 1520 | 1030 |
| f | 3030 | 1600 | 1540 | 1020 |
| g | 3000 | 1595 | 1510 | 1020 |
| h | 3015 | 1000 | 1540 | 1005 |
| i | 3000 | 1600 | 1545 | 1030 |
| j | 3010 | 1600 | 1540 | 1015 |
| k | 3000 | 1600 | 1545 | 1035 |
| l | 3015 | 1605 | 1540 | 1010 |
| m | 3010 | 1600 | 1490 | 1030 |
| n | 3010 | 1600 | 1515 | 1030 |
| o | 3020 | 1590 | 1530 | 1005 |
| p | 3030 | 1595 | 1540 | 998 |
| q | 3010 | 1600 | 1535 | 1005 |
| r | 3000 | 1600 | 1515 | 1025 |

ν = Stretching vibrations; ϕ = Out of plane deformation of hydrogen attached to aromatic nucleus.

TABLE III.3. NMR(CDCl₃) DATA OF 2,4,6-TRIARYLPYRIDINES (5a-r)

| Compound | δ (ppm) | No. of protons | Assignment to protons |
|----------|----------------|----------------|----------------------------------|
| 5a | 3.64-3.82, d | 6H | (OCH ₃) ₂ |
| | 6.63-8.02, m | 14H | Ar-H+PyH |
| b | 3.74, s | 3H | OCH ₃ |
| | 6.65-8.03, m | 14H | Ar-H+PyH |
| c | 3.88, s | 9H | (OCH ₃) ₃ |
| | 6.96-8.21, m | 14H | Ar-H+PyH |
| d | 3.70, s | 3H | OCH ₃ |
| | 3.10, s | 6H | N(CH ₃) |
| | 6.80-8.05, m | 14H | Ar-H+PyH |
| e | 3.70, s | 3H | OCH ₃ |
| | 3.85, d | 6H | (OCH ₃) ₂ |
| | 6.95-8.10, m | 13H | Ar-H+PyH |
| f | 3.75, s | 6H | (OCH ₃) ₂ |
| | 6.85-8.05, m | 14H | Ar-H+PyH |
| g | 3.80, s | 6H | (OCH ₃) ₂ |
| | 3.10, s | 6H | N(CH ₃) ₂ |
| | 6.90-8.15, m | 14H | Ar-H+PyH |
| h | 3.82-4.06, m | 12H | (OCH ₃) ₄ |
| | 6.88-8.19, m | 13H | Ar-H+PyH |
| i | 3.75, d | 6H | (OCH ₃) ₂ |
| | 5.95, s | 2H | O ₂ CH ₂ |
| | 7.05-8.15, m | 13H | Ar-H+PyH |

CONTD. III.3.

| 1 | 2 | 3 | 4 |
|---|--------------|-----|----------------------------------|
| j | 3.78, s | 3H | OCH ₃ |
| | 6.05, s | 2H | O ₂ CH ₂ |
| | 6.88-8.20, m | 13H | Ar-H+PyH |
| k | 2.35, s | 3H | CH ₃ |
| | 3.72, s | 3H | OCH ₃ |
| | 5.98, s | 2H | O ₂ CH ₂ |
| | 7.15-8.10, m | 13H | Ar-H+PyH |
| l | 2.33, s | 3H | CH ₃ |
| | 3.64-3.78, d | 6H | (OCH ₃) ₂ |
| | 6.60-8.08, m | 14H | Ar-H+PyH |
| m | 3.80, s | 3H | OCH ₃ |
| | 7.15-8.35, m | 18H | Ar-H+PyH |
| n | 3.65, s | 3H | OCH ₃ |
| | 2.38, s | 3H | CH ₃ |
| | 7.15-8.25, m | 17H | Ar-H+PyH |
| o | 3.70, s | 3H | OCH ₃ |
| | 3.85, d | 6H | (OCH ₃) ₂ |
| | 7.10-8.20, m | 12H | Ar-H+PyH |
| p | 2.40, s | 3H | CH ₃ |
| | 3.85, d | 6H | (OCH ₃) ₂ |
| | 3.70, s | 3H | (OCH ₃) |
| | 7.00-8.15, m | 13H | Ar-H+PyH |

CONTD. Table III.3.

| 1 | 2 | 3 | 4 |
|---|--------------|-----|----------------------------------|
| q | 3.75, s | 3H | OCH ₃ |
| | 7.15-8.25, m | 20H | Ar-H+PyH |
| r | 3.70, s | 3H | OCH ₃ |
| | 3.88, d | 6H | (OCH ₃) ₂ |
| | 6.88-8.15, m | 13H | Ar-H+PyH |

s = Singlet;

d = Doublet;

m = Multiplet

CHAPTER IV

CHAPTER-IV

SYNTHESIS OF 2,4,6-TRISUBSTITUTED PHENYL PYRIMIDINES USING 4-NITROPHENACYL DIMETHYL SULFURANE AND 4-FLUOROPHENACYL DIMETHYL SULFURANE WITH AROMATIC ALDEHYDES.

IV.1. ABSTRACT :

4-Nitrophenacyl dimethyl sulfonium bromide and 4-fluorophenacyl dimethyl sulfonium bromide have been prepared by the reaction of dimethyl sulphide with 4-substituted phenacylbromide in benzene at reflux temperature in good yields. These sulfonium salts on treatment with NaOH gave corresponding 4-nitrophenacylidene dimethyl sulfurane and 4-fluorophenacylidene dimethyl sulfurane. Reaction of these sulfonium salts and sulfuranes with various aromatic aldehydes was carried out in presence of ammonium acetate and acetic acid at reflux temperature in an atmosphere of nitrogen gave 2,4,6-triaryl pyrimidine in 35-80% yields. Ammonium acetate in acetic acid was used as azacyclization agent. The structures of new pyrimidines were confirmed on the basis of IR and NMR spectra data.

IV.2. INTRODUCTION :

Pyridinium, phosphonium, arsonium and isoquinolinium have gained considerable importance in the synthesis of acyclic, cyclic and heterocyclic compounds¹⁻⁷ (Scheme IV.1). Noteworthy in this regards are the synthesis of pyridines¹⁻², Indoles³,

Tetrazines⁴, Cinnolines⁵, Napthalenes⁶, Epoxides⁷, Cyclopropanes⁷ and azaridines⁷ and several other heterocycles. As reported earlier sulfonium salts and π -sulfuranes are better potential reagents than corresponding ylides of V group elements for the synthesis of heterocycles⁸⁻¹⁵ Krohnke¹⁶ first time reported in a single reaction involving condensation of phenacylpyridinium bromide with 4-nitrobenzaldehyde to yield 2,4-di-(4-nitrophenyl)-6-phenylpyrimidine. Detail experimental conditions were also not reported by Krohnke's et al¹⁶. Further more reaction of pyridinium ylides was not explored and duplicated with other aromatic aldehydes until recently. As in the several cases sulfonium and pyridinium ylides follows the same course of reaction¹⁻¹⁷. Hence further extension of reaction leading to the pyrimidine nucleus seems to be pertinent. With a view the test of domain of applicability of sulfonium salts and π -sulfuranes. In the present chapter 4-nitrophenacyldimethyl-sulfonium bromide and 4-fluorophenacyldimethyl sulfonium bromide as well as their corresponding π -sulfuranes have been coupled with a wide range of aromatic aldehydes in presence of ammonium acetate and acetic acid at reflux temperature leading to aza ring closure to form pyrimidine nucleus.

IV.3. RESULTS & DISCUSSION :

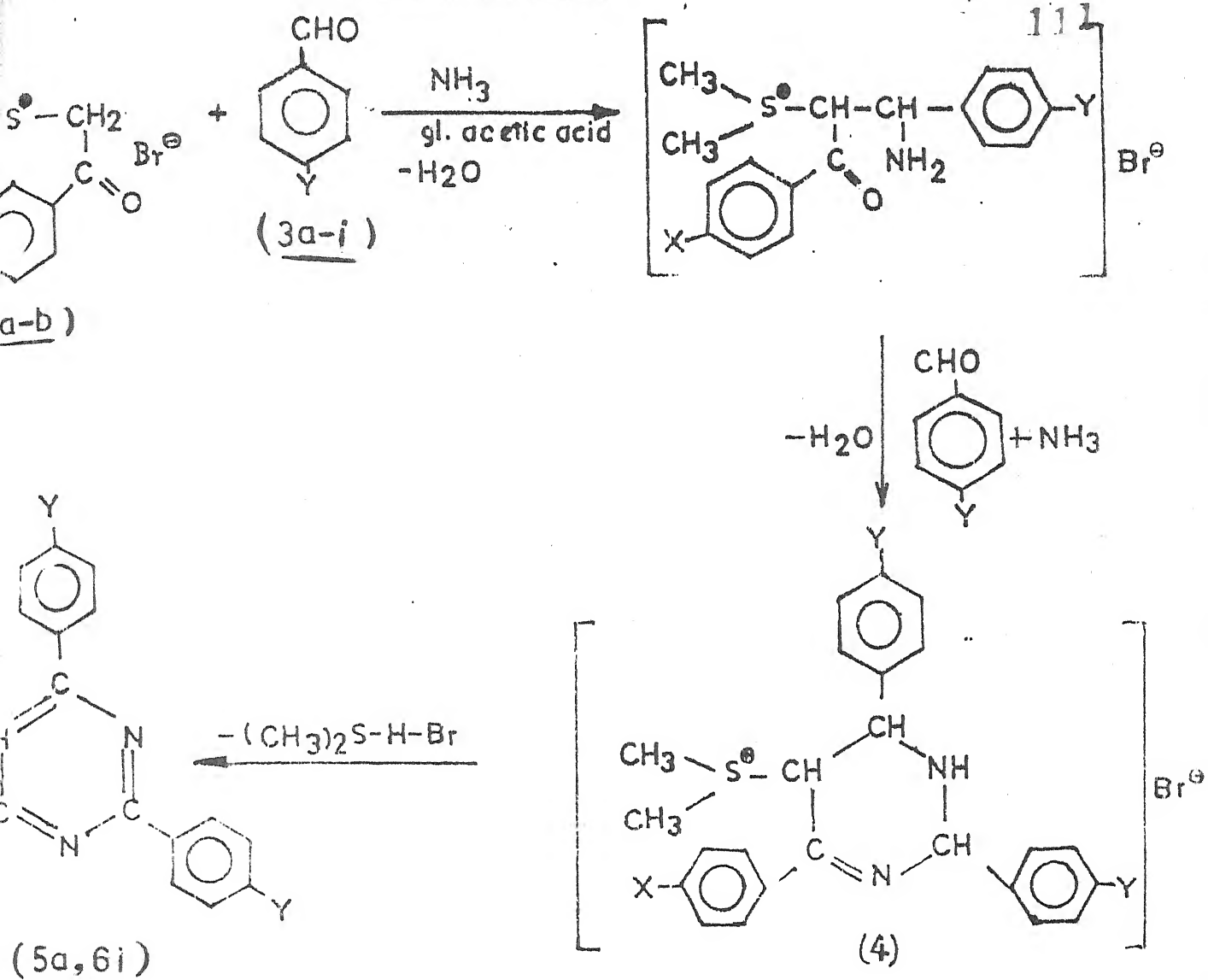
Reaction of dimethyl sulfide with 4-nitrophenacyl

bromide and 4-fluorophenacyl bromide in benzene at reflux temperature gave 4-nitrophenacyldimethyl sulfonium bromide (1a) 4-fluorophenacyl dimethyl sulfonium bromide (1b) in fair to good yields. The structure of sulfonium salts (1a-b) were confirmed by comparison of melting points of salts with those reported in the literature^{15,17} and by spectral data. The IR spectra of salts (1a-b) showed a characteristic absorption band due to C=O stretching vibrations in the region 1670-1690 cm^{-1} for carbonyl group. The diagnostic absorption bands in the region 3300-3000 cm^{-1} were observed due to C-H stretching vibrations of methylene group attached to sulfur atom^{18,19}.

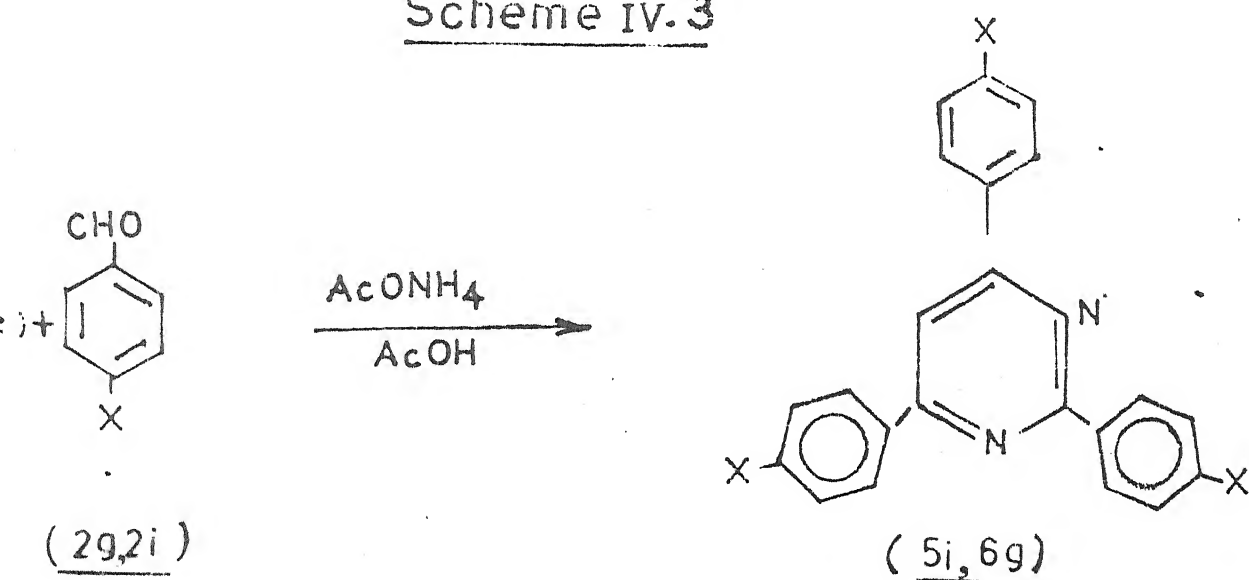
The treatment of these salts (1a-b) with aqueous sodium hydroxide/potassium carbonate gave 4-nitrobenzylidene dimethyl sulfurane (2a) and 4-fluorobenzylidene dimethyl sulfurane (2b) which could not be stored due to sensitivity towards atmospheric components and lack of stabilizing factors. Hence they could not be used in subsequent reactions. The reaction was therefore carried out by generating the ylide intermediates (2a-b) in situ from the corresponding salts (1a-b).

Heating the mixture of sulfonium salts (1a-b) with substituted benzaldehyde (3a-i) in presence of ammonium acetate and glacial acetic acid at reflux temperature gave 2,4,6-triaryl pyrimidines (5a-i, 6a-i) 35-80% yields (Scheme IV.2).

Scheme IV.2



Scheme IV.3



Further attempts were made to synthesize symmetrical pyrimidines having identical substituents at 2,4,6-positions. For this purpose 4-nitrophenacyldimethyl sulfonium bromide (1a) with 4-nitrobenzaldehyde and 4-fluorophenacyl dimethyl sulfonium bromide (1b) with 4-fluorobenzaldehyde were heated in a mixture of ammonium acetate and glacial acetic acid to give corresponding symmetrical pyrimidines viz. 2,4,6-tri-(4-nitrophenyl) pyrimidines (5i) and (4-fluorophenyl) pyrimidines (6g) respectively in 65-60% yields (Scheme IV.3).

The reaction takes place through Mannich type reaction. The methylene group of salt (1a-b) with aromatic aldehydes (3a-i) in presence of ammonium acetate forms Mannich base-sulfonium salt (3) which in turn, undergoes condensation with another molecule of benzaldehyde in presence of ammonia to form sulfonium salt intermediate (4). The later, then undergoes elimination of dimethyl sulfonium hydrobromide to form 2,4,6-triaryl pyrimidines (5a-i, 6a-i).

A number of 2,4,6-triaryl pyrimidines (5a-i) and (6a-i) synthesized by the above route are new and listed in table IV.1. All the pyrimidines gave satisfactory elemental and spectral analysis. The IR spectral data (Table IV.2) showed a characteristic absorption bands in the region 3100cm^{-1} - 3000cm^{-1} which were assigned due to C-H stretching mode of pyrimidine ring. The bands in the region 1600 - 1500cm^{-1} were due to

interaction between C=C and C=N vibrations of the ring. The NMR spectra (table IV.3) of pyrimidines showed pyrimidal proton (C_5-H) in the range δ 6.40-6.80 and aromatic protons at δ 6.60-8.40.

IV.4. EXPERIMENTAL :

IV.4.1. Starting Material :

All the reagents were obtained from commercial source (E. Merck, BDH, SISCO etc.). Starting materials viz. 4-nitrophenacyl bromide and 4-fluorophenacyl bromide were prepared according to the procedure reported in literature²⁰.

IV.4.2. Preparation of 4-nitrophenacyl dimethyl sulfonium bromide(1a) :

A solution of 100m mole of 4-nitrophenacyl bromide and 100m mole of dimethyl sulfide in 100ml of anhydrous acetone was stirred for 6-8 hrs. at room temperature in an atmosphere of nitrogen gave solid mass which was filtered, washed twice with acetone and crystallized from benzene pet. ether. The compound which was obtained has yellow coloured micro crystals m.p. 150-152°C (Lit.¹⁵ m.p. 152-154°C).

IR data (KBr): 1680cm^{-1} ($\nu_{C=O}$) $1570, 1330\text{cm}^{-1}$ (ν_{C-NO_2})

NMR(CDCl_3): δ 3.30(s, 6H, di CH_3): δ 5.50(s, 2H, $\underline{\text{CH}_2}$):

δ 7.30-7.90(m, 4H, Ar-H)

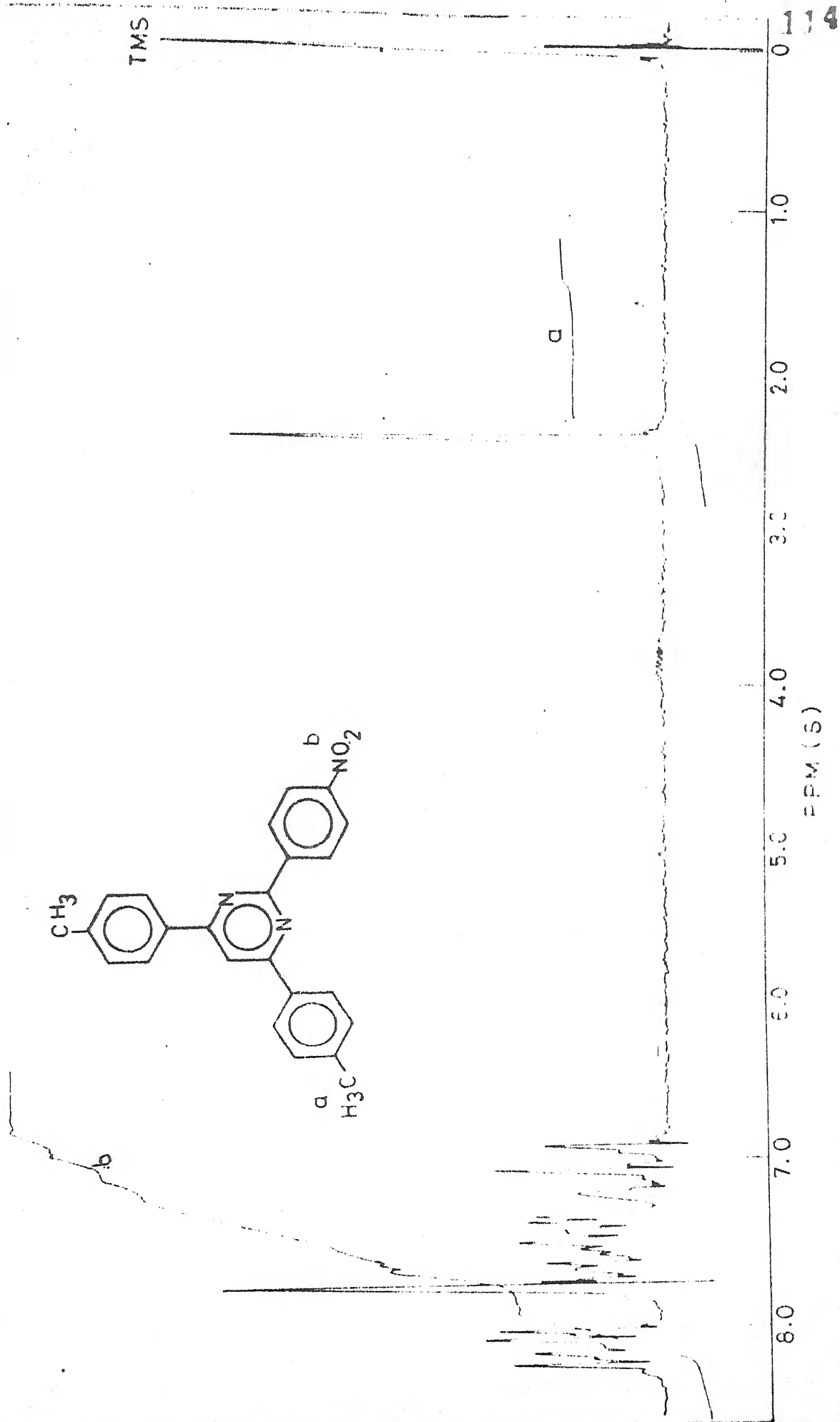


FIG. IV. 1 NMR SPECTRUM OF **5b**.

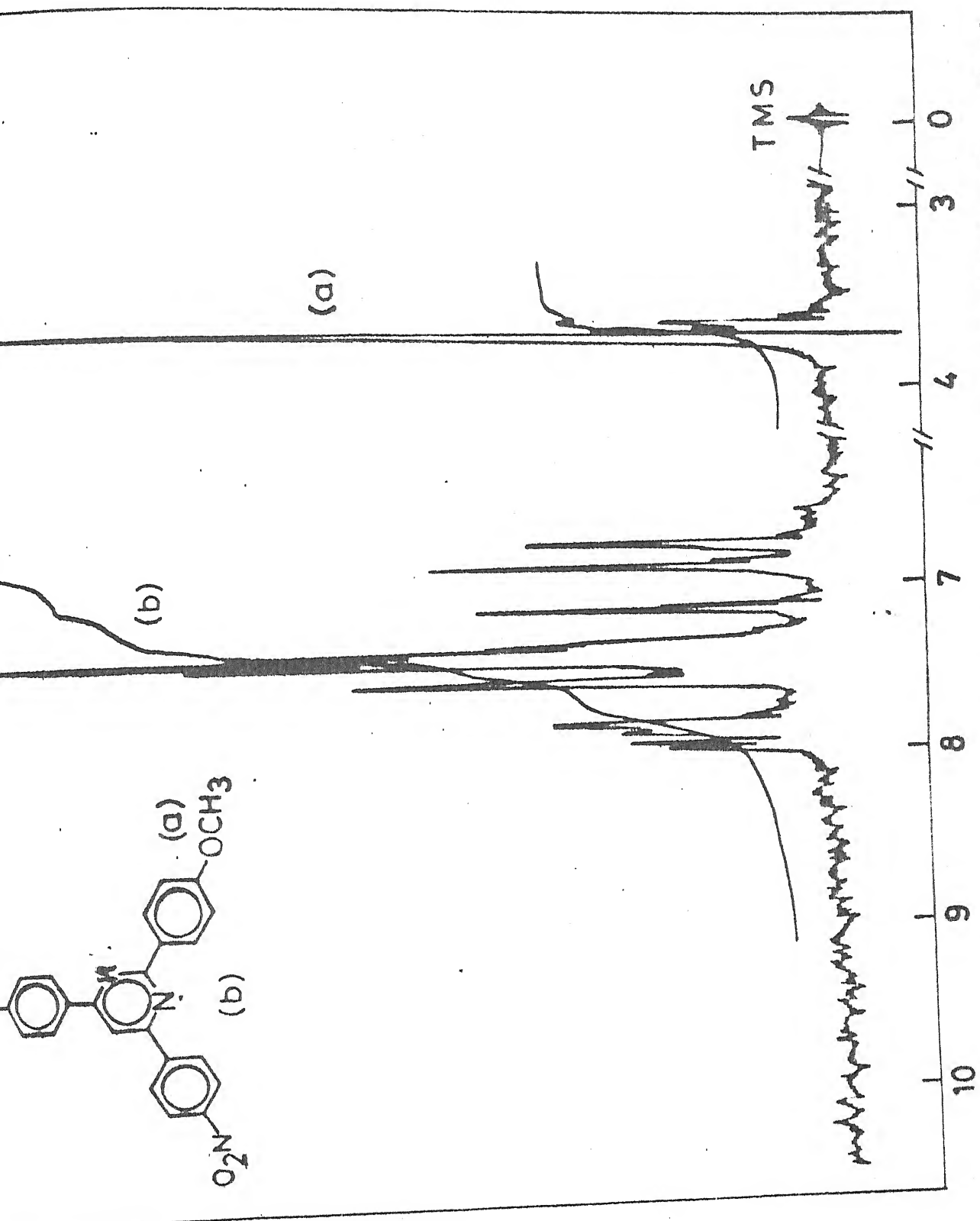


FIG. IV.2 NMR SPECTRUM OF COMPOUND (5d)

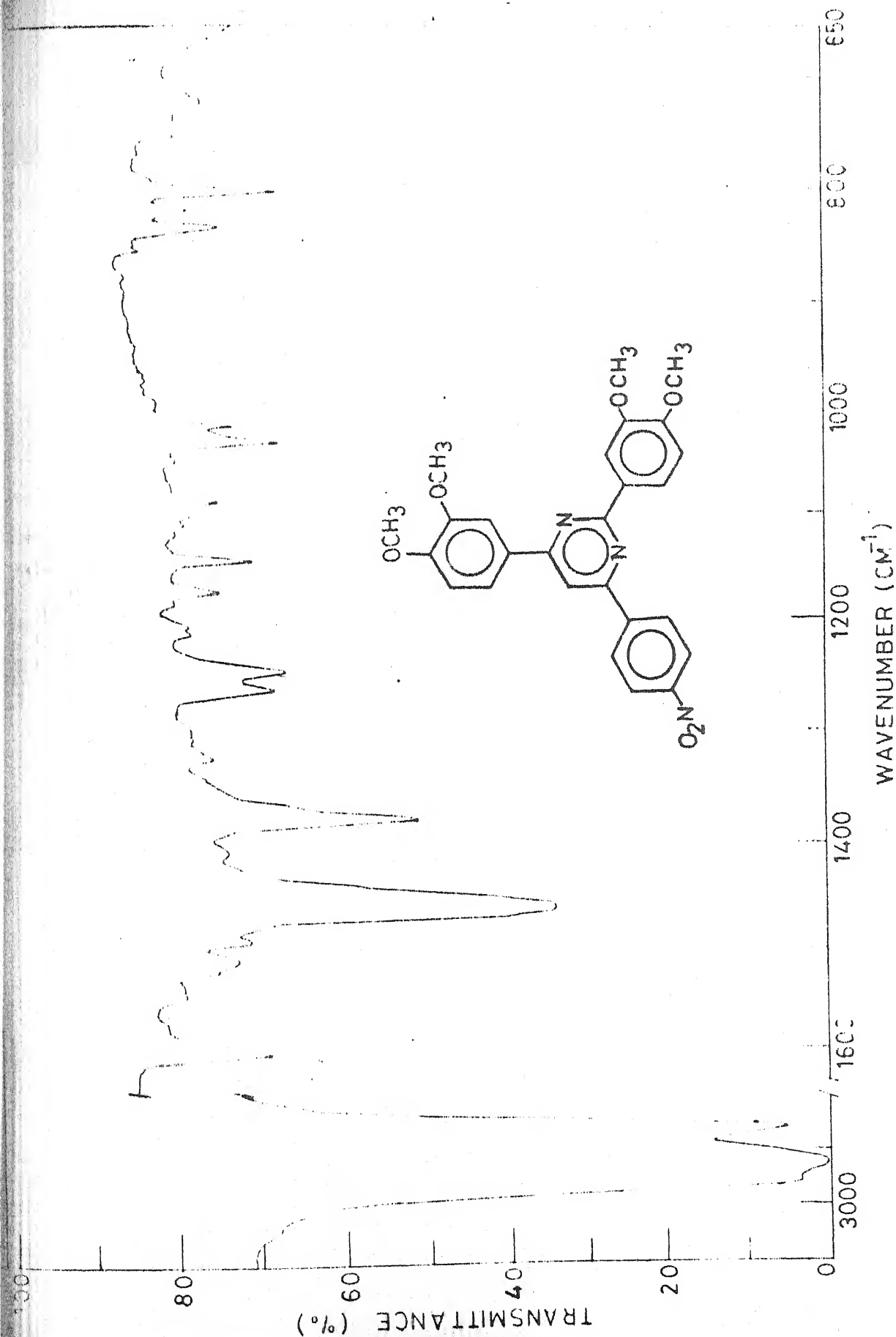
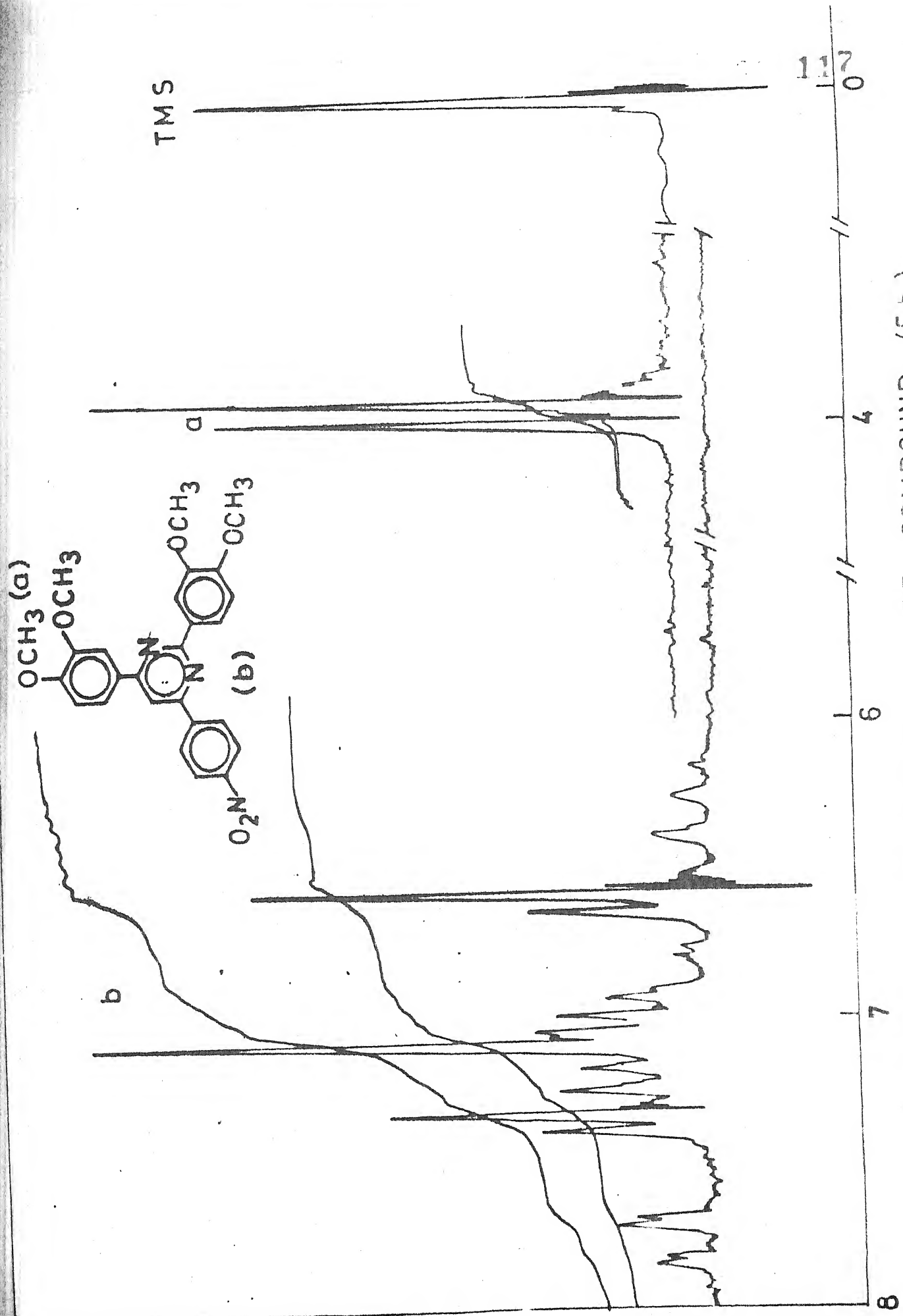


FIG.IV.3 IR SPECTRUM OF **5h**



FIGIV. 4 3 SPECT OF COMPOUND (5b)

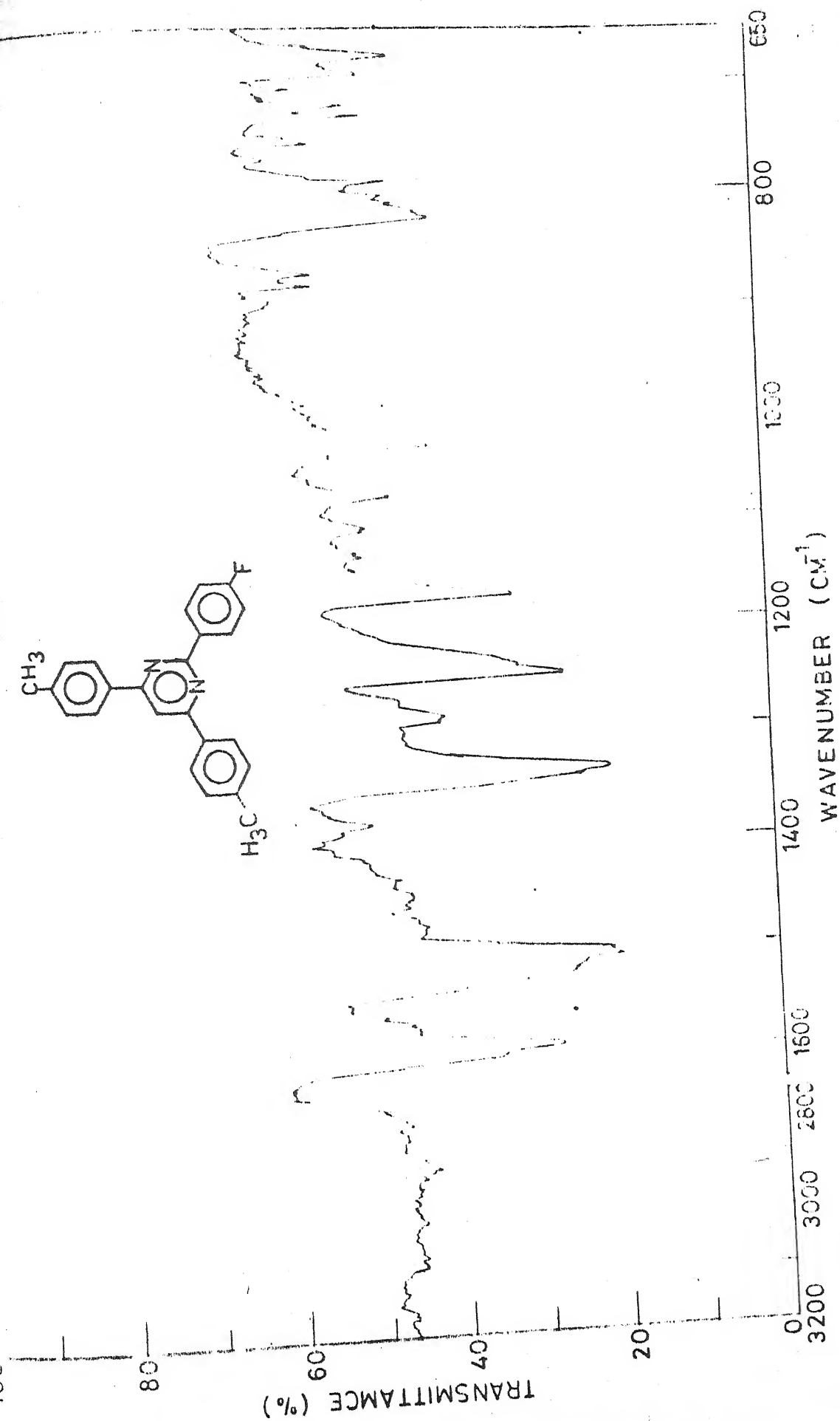


FIG. IV.5 IR SPECTRUM OF 6b .

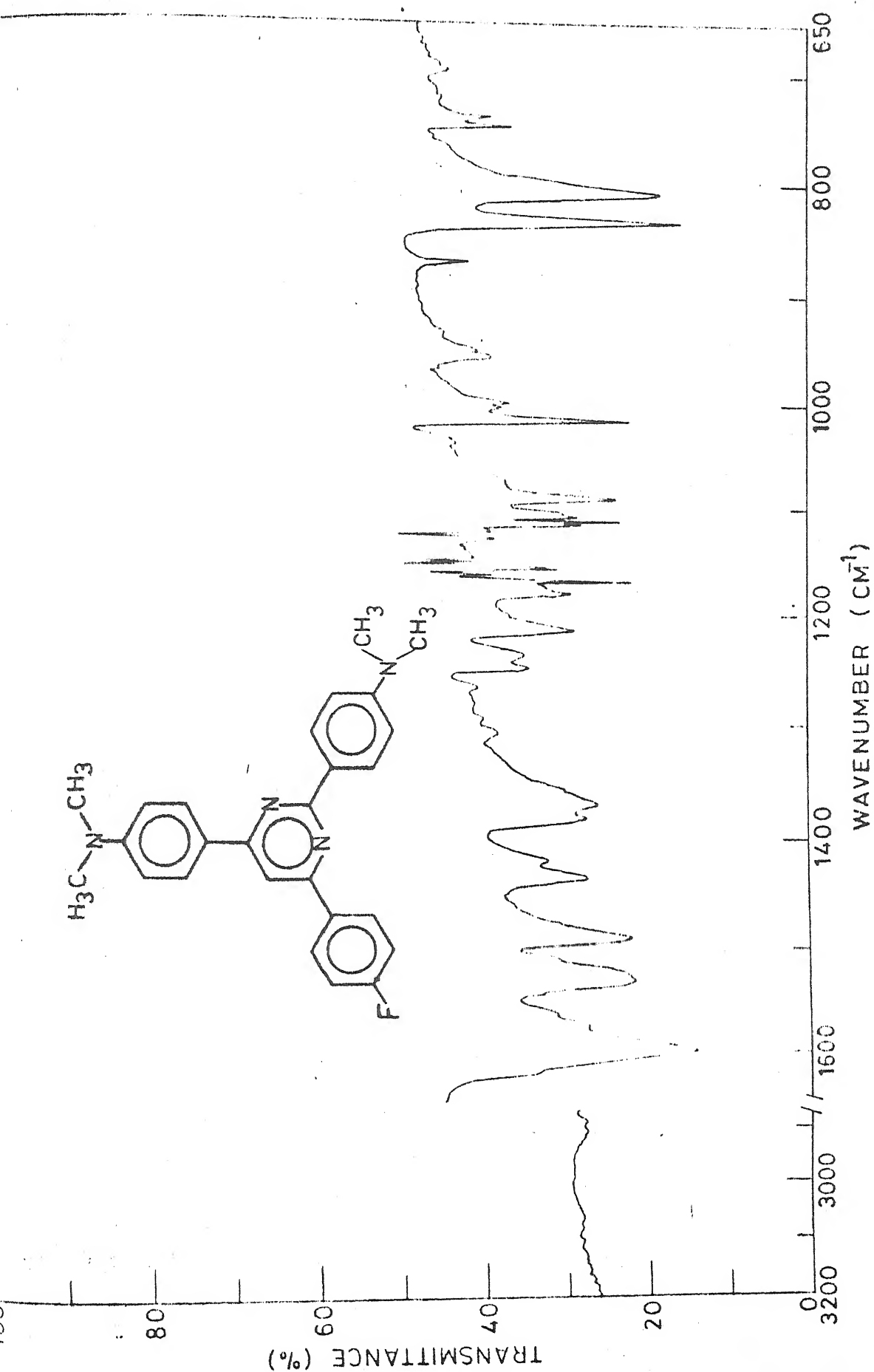
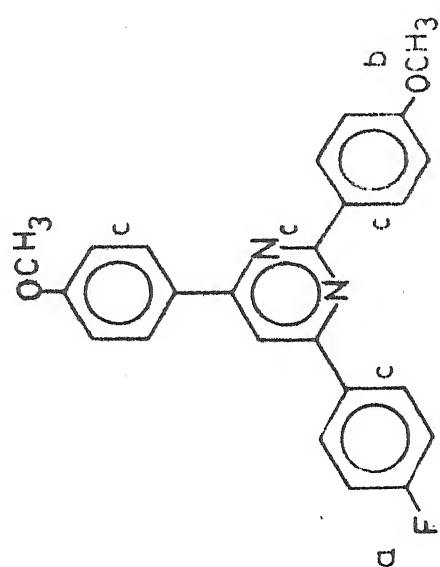


FIG. IV.6 IR SPECTRUM OF **6c**.



PPM (S)

FIG. IV. 7 NMR SPECTRUM OF 6d.

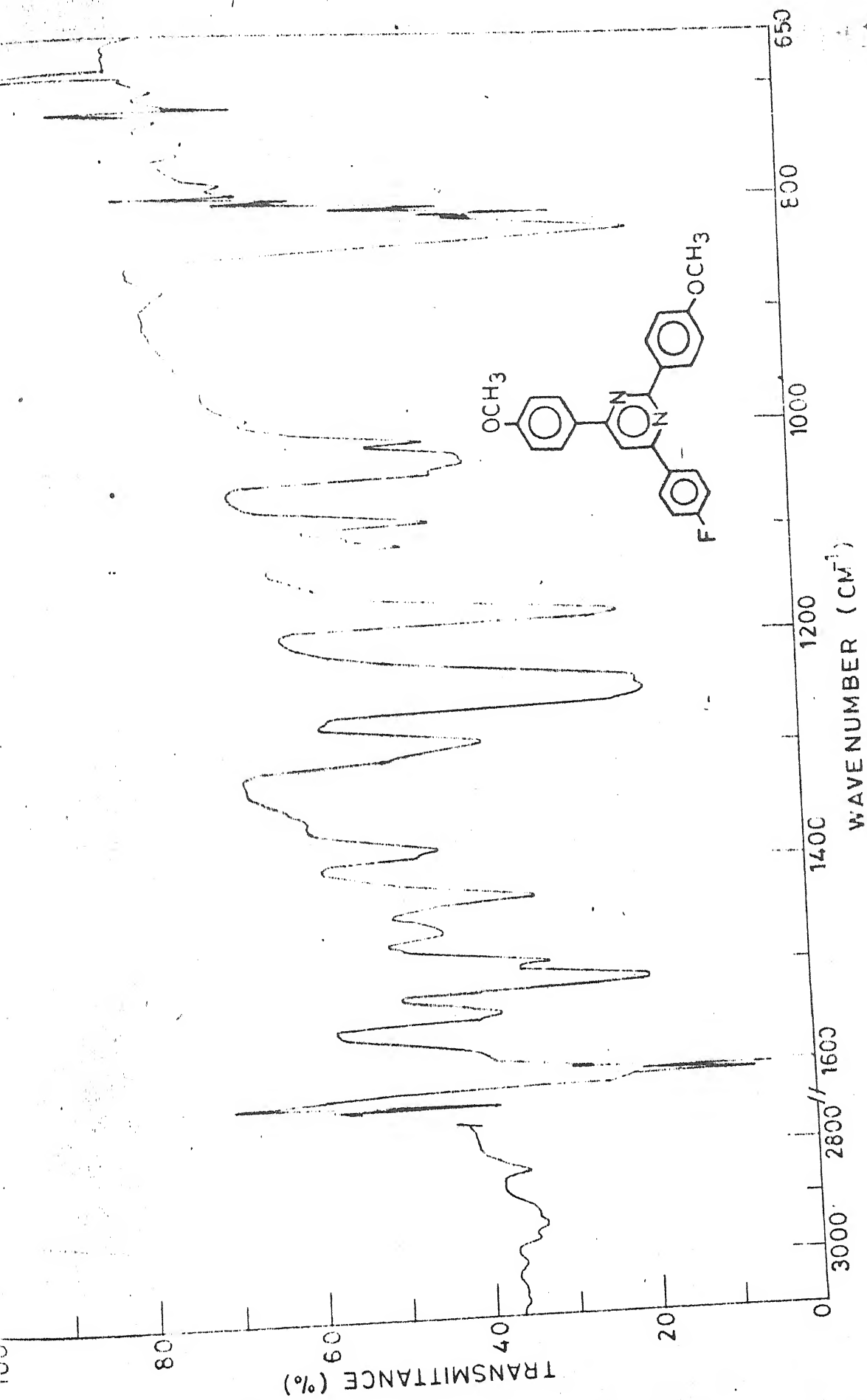


FIG. IV.8 IR SPECTRUM OF 6d

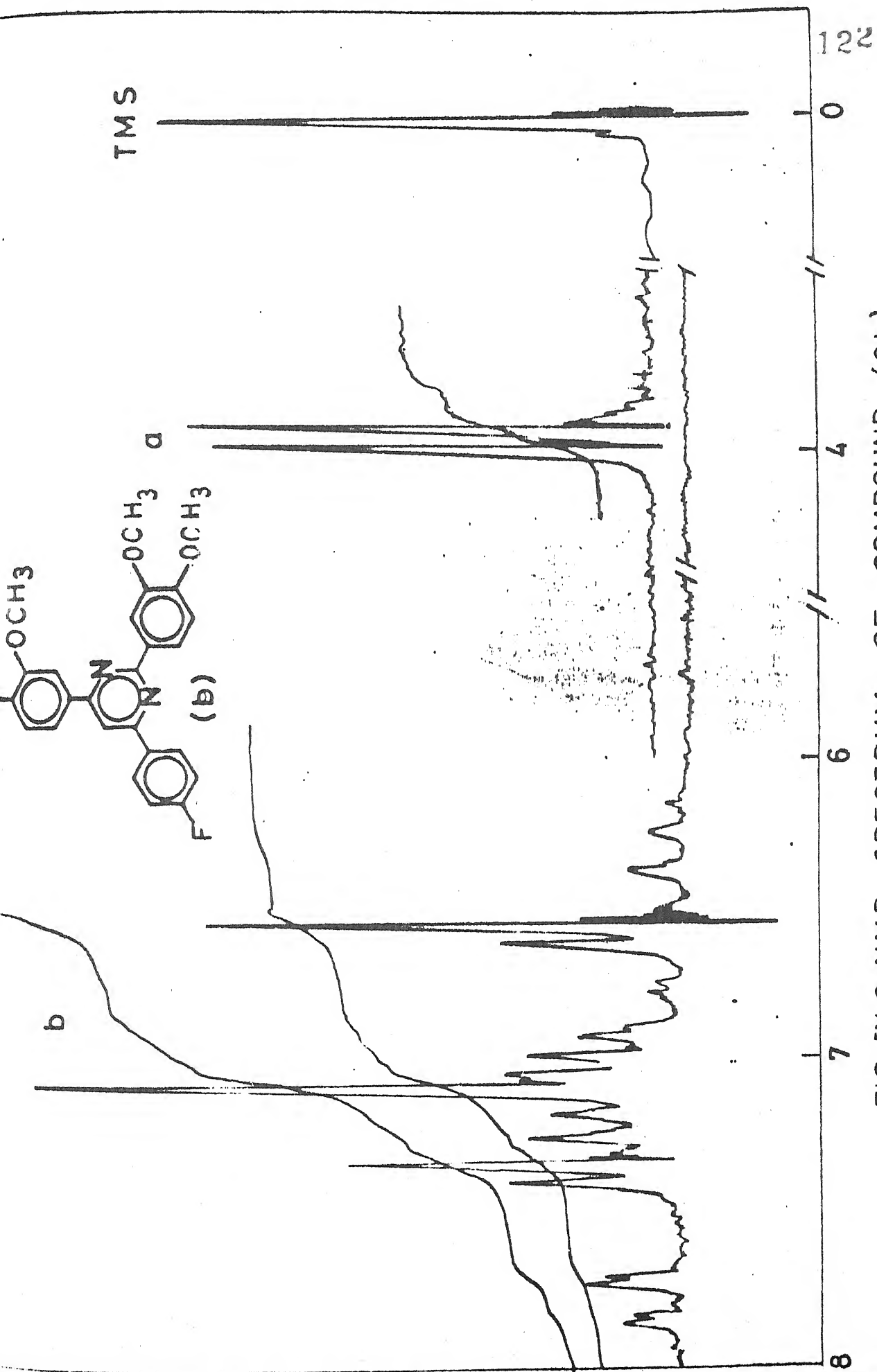


FIG. IV-9 NMR SPECTRUM OF COMPOUND (6h)

IV.4.3. Preparation of 4-nitrophenacylidenedimethyl sulfurane (2a) :

4-Nitrophenacylidenedimethyl sulfonium bromide(1a) (50m mole) was dissolved in water (30ml). The coloured suspension was filtered and the clear filtrate was treated with 10% aq. NaOH (15ml). The solution was stirred for 8 hrs under nitrogen atmosphere and then extracted several time with CHCl_3 . The chloroform extract was dried with sodium sulphate and evaporated to give yellow oil which on cooling gave yellow solid. The yellow solid on crystallization with ethanol afforded reddish yellow crystal of 4-nitrophenacylidene dimethyl sulfurane(2a) in 85% yield. Which melted at $64-66^\circ\text{C}$ (Lit.¹⁵ m.p. $66-68^\circ\text{C}$).

IR data (KBr) max.: 3020cm^{-1} ($\nu\text{C-H}$) : 1670cm^{-1} ($\nu\text{C=O}$)

NMR(CDCl_3) (δ ppm) : 3.20(s, 6H, di CH_3) 5.50(s, 2H, CH_2) :

7.35-8.90(m, 4H, ArH)

IV.4.4. Preparation of 4-fluorophenacyl bromide (1b) :

Stirring a mixture of 4-fluorophenacyl bromide(0.1 mole) and dimethyl sulfide (30ml) for 8 hrs gave white solid mass. The solid mass was filtered, washed twice with ether and recrystallized from alcohol as white colourless microcrystals m.p. $140-142^\circ\text{C}$ (Lit.¹⁷ m.p. $142-144^\circ\text{C}$).

IR data (KBr) max: 3100 (ArH), 1675cm^{-1} ($\nu\text{C=O}$)

NMR(CDCl_3) (δ ppm) : 3.26(s, 6H, di CH_3) : 5.45(s, 2H, CH_2) :

7.25-7.85 (m, 4H, ArH).

IV.4.5. Preparation of 4-fluorophenacylidene dimethyl sulfurane (2b):

4-Fluorophenacyl dimethyl sulfonium bromide (1b) (50m mole) was dissolved in water (30ml). The coloured suspension was filtered with 10% aq. NaOH (15ml). The solution was stirred for 8 hrs and then extracted several times with CHCl_3 . The chloroform extract was dried with sodium sulphate and evaporated to give light yellow oil which on cooling gave light yellow solid. The light yellow solid on crystallization with ethanol afforded light reddish yellow crystals of 4-fluorophenacylidene dimethyl sulfurane (2) in 85% yields which melted at $68-69^\circ\text{C}$ (Lit.¹⁷ m.p. $69-70^\circ\text{C}$).

IR data (KBr) max: 2980 (Ar-H); 1520 cm^{-1} ($\nu\text{C=O}$)

NMR (CDCl_3) (δ ppm): 3.16(s, 6H, di CH_3): 4.31(s, 1H, $\underline{\text{CH}_2}$):

7.28-7.97(m, 4H, ArH)

IV.4.6. Preparation of 2,4,6-triaryl pyrimidines (5a-i, 6a-i):

General Procedure :

A mixture of 3m mole 4-substituted phenacyl dimethylsulfonium bromide (1a-b) and 6m mole of aromatic aldehyde (2) and 3gm of ammonium acetate in 50ml of glacial acetic acid was stirred at room temperature. The mixture was then poured in ice cold water (50ml) which was constantly stirred. The solid mass was precipitated, filtered and washed

twice with water and then with methanol and dried. The product, on crystallization with appropriate solvents, gave crystalline 2,4,6-triarylpyrimidine(5a-i) & (6a-i) in good yields as computed in table IV.1.

REFERENCES

1. R.S. Tewari and A.K. Awasthi, *Synthesis*, 94, 314 (1981).
2. K.C. Gupta, P.K. Pathak, B.K. Saxena, N. Srivastava and Kalpana Pandey, *J.Chem. & Engg.Data*, 32, 131 (1987).
3. H. Junjappa, *Synthesis* (12), 798 (1975).
4. R.S. Tewari, A.K. Awasthi, Padma Parihar, *Synthesis*(4), 334 (1983).
5. R.K. Bansal, S.K. Sharma and G. Bhagchandani, *Indian J. Chem.*, 21B, 149 (1982).
6. K.C. Gupta, B.K. Saxena, P.K. Pathak and N. Srivastava, *Curr.Sci.*, 54, 571 (1985).
7. R.S. Tewari, A.K. Awasthi and Anita Awasthi, *Synthesis*(4), 330 (1983).
8. A.K. Tschitschibabin, *Bull Soc.Chem.*, 4, 1826 (1937); *J. Russ.Chem.Soc.*, 37, 1229 (1905); *J.Prakt.Chem.*, 107, 122 (1924).
9. R.L. Frank and R.P. Seven, *J.Amer.Chem.Soc.*, 21, 2629 (1949).
10. R.L. Frank and E.F. Piever, *J.Amer.Chem.Soc.*, 72, 4182 (1950).
11. F. Krohnke and W. Zecher, *Angew Chem.Int.Ed.*, 1, 626(1962); *Chem.*, 94, 690 (1961); 95, 1128 (1962).

12. F. Krohnke, *Synthesis*, 1 (1926).
13. K.C. Gupta, N. Srivastava and R.K. Nigam, *J.Organomet. Chem.*, 204, 55 (1981).
14. R.K. Bansal and G. Bhagchandani, *Indian J.Chem.*, 18B, 362 (1979).
15. W.G. Phillips and K.W. Ratts, *J.Org.Chem.*, 35, 3144(1970).
16. F. Krohnke and K. Ellegast, *Chem.Ber.*, 86, 1554 (1970).
17. K.C. Gupta, P. Manglam, *J.Chem.Engg.data*, 32, 131(1987).
18. L.J. Bellamy, "The Infrared spectra of complex molecules", Wiley, New York, pp 271-81 (1954).
19. G.L. Cook and F.M. Church, *J.Phys.Chem.*, 61, 458 (1957).
20. H. Gilman and A.H. Blatt, *Org.Syn.*, 1, 78 (1958).

TABLE IV.1. PHYSICAL PROPERTIES OF 2,4,6-TRIARYLPYRIDINES (5a-i, 6a-i)

| Compound | X | Y | yield % | M.P. °C | Recry- stn. Solvent | Analysis found/(calcd.) | | |
|----------|-------------------|------------------------------------|---------|------------|---------------------------|-------------------------|----------------|------------------|
| | | | | | | C% | H% | N% |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 5a | 4-NO ₂ | H | 45 | 110-12 | A | 74.02 (74.05) | 4.35 (4.37) | 12.20 (12.24) |
| b | 4-NO ₂ | 4-CH ₃ | 40 | 96-98 | B | 75.61 (75.59) | 4.93 (4.98) | 11.04 (11.02) |
| c | 4-NO ₂ | 4-N(CH ₃) ₂ | 45 | 120-22 | A | 71.03 (71.07) | 5.67 (5.69) | 15.99 (15.95) |
| d | 4-NO ₂ | 4-OCH ₃ | 60 | 128-30 | C | 69.70 (69.73) | 4.62 (4.60) | 10.14 (10.16) |
| e | 4-NO ₂ | 4-Cl | 65 | 78-80 | A | 62.54 (62.56) | 3.04 (3.08) | 10.07 (10.05) |
| f | 4-NO ₂ | 4-Br | 55 | 86-88 | B | 55.76 (55.81) | 2.71 (2.75) | 8.82 (8.88) |
| g | 4-NO ₂ | 4-F | 65 | 110-12 | C | 67.80 (67.87) | 3.36 (3.34) | 9.27 (9.26) |
| h | 4-NO ₂ | 3,4-di(OCH ₃) | 48 | 122-24 | A | 70.40 (70.42) | 5.68 (5.64) | 9.42 (9.48) |
| i | 4-NO ₂ | 4-NO ₂ | 80 | 132-34 | C | 59.55 (59.59) | 2.90 (2.93) | 15.82 (15.80) |

CONTD. Table IV.1.

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|----|-----|------------------------------------|----|--------|---|------------------|----------------|------------------|
| 6a | 4-F | H | 48 | 98-10 | D | 80.92 (80.98) | 4.62 (4.60) | 11.62 (11.64) |
| b | 4-F | 4-CH ₃ | 45 | 112-14 | B | 81.34 (81.36) | 5.37 (5.37) | 7.92 (7.90) |
| c | 4-F | 4-N(CH ₃) ₂ | 41 | 124-26 | C | 75.70 (75.72) | 6.06 (6.07) | 13.52 (13.59) |
| d | 4-F | 4-OCH ₃ | 42 | 130-32 | A | 78.42 (78.47) | 5.15 (5.17) | 7.64 (7.62) |
| e | 4-F | 4-Cl | 50 | 76-78 | C | 66.80 (66.84) | 3.26 (3.29) | 7.05 (7.08) |
| f | 4-F | 4-Br | 55 | 88-90 | A | 57.80 (57.85) | 2.67 (2.69) | 5.75 (5.79) |
| g | 4-F | 4-F | 60 | 108-10 | B | 72.90 (72.93) | 3.52 (3.59) | 7.70 (7.73) |
| h | 4-F | 3,4-di(OCH ₃) | 50 | 124-26 | A | 69.94 (69.99) | 5.13 (5.15) | 6.24 (6.28) |
| i | 4-F | 4-NO ₂ | 45 | 128-30 | C | 63.42 (63.46) | 3.10 (3.12) | 13.42 (13.46) |

A = CH₃OH • CHCl₃

B = C₆H₆ : CHCl₃

C = C₅H₅N : CH₃OH

TABLE IV.2. IR DATA (KBr) Cm^{-1} 2,4,6-TRIARYLPYRIMIDINES
(5a-i, 6a-i)

| Compound | IR Data (KBr) Cm^{-1} | | | | |
|----------|--------------------------------|-----------|-----------|------------|-------------------------|
| | ν C-H | ν C=C | ν C=N | ϕ C-H | ν C-NO ₂ |
| 5a | 3110 | 1605 | 1510 | 995 | 1555, 1325 |
| b | 3085 | 1615 | 1525 | 990 | 1575, 1330 |
| c | 3105 | 1605 | 1510 | 995 | 1580, 1335 |
| d | 3115 | 1610 | 1520 | 992 | 1585, 1335 |
| e | 3060 | 1608 | 1505 | 990 | 1580, 1340 |
| f | 3110 | 1595 | 1500 | 1000 | 1575, 1320 |
| g | 3080 | 1598 | 1505 | 1005 | 1570, 1325 |
| h | 3108 | 1605 | 1510 | 1000 | 1580, 1330 |
| i | 3070 | 1610 | 1510 | 1005 | 1575, 1320 |
| 6a | 3090 | 1600 | 1505 | 998 | 1580, 1335 |
| b | 3105 | 1605 | 1510 | 1005 | 1580, 1335 |
| c | 3100 | 1615 | 1500 | 992 | 1560, 1330 |
| d | 3065 | 1598 | 1500 | 1000 | 1570, 1330 |
| e | 3080 | 1605 | 1510 | 1010 | 1580, 1335 |
| f | 3100 | 1615 | 1505 | 992 | 1580, 1320 |
| g | 3105 | 1614 | 1505 | 995 | 1560, 1340 |
| h | 3080 | 1600 | 1500 | 998 | 1575, 1330 |
| i | 3095 | 1608 | 1505 | 990 | 1560, 1320 |

ν = Stretching vibrations; ϕ = Out of plane deformation of hydrogen attached to aromatic nucleus.

TABLE IV.3. NMR (CDCl₃) DATA OF 2,4,6-TRIARYLPYRIMIDINES (5a-i, 6a-i)

| Cmpound | δ (ppm) | No. of protons | Assignment to protons |
|---------|-------------------------------|----------------|--------------------------------------|
| 1 | 2 | 3 | 4 |
| 5a | 6.65, s | 1H | PyH (C ₅ -H) |
| | 6.85-6.88, m | 14H | Ar-H |
| b | 6.65, s | 1H | PyH (C ₅ -H) |
| | 2.35, s | 6H | di CH ₃ |
| | 6.95-8.20, m | 12H | Ar-H |
| c | 6.65, s | 1H | PyH (C ₅ -H) |
| | 3.95, s | 12H | di N-(CH ₃) ₂ |
| | 6.75-7.85, m | 12H | Ar-H |
| d | 6.66, s | 1H | PyH (C ₅ -H) |
| | 3.85, s | 6H | di (OCH ₃) |
| | 6.95-8.35, m | 12H | Ar-H |
| e | 6.78, s | 1H | PyH (C ₅ -H) |
| | 7.0-8.25, m | 12H | Ar-H |
| f | 6.80, s | 1H | PyH (C ₅ -H) |
| | 6.95-8.20, m | 12H | Ar-H |
| g | 6.75, s | 1H | PyH (C ₅ -H) |
| | 7.10-8.35, m | 12H | Ar-H |
| h | 6.65, s | 1H | PyH (C ₅ -H) |
| | 3.95, d, (J=6H ₂) | 12H | di(3,4-di OCH ₃) |
| | 6.85-7.05, m | 10H | Ar-H |
| i | 6.75, s | 1H | PyH (C ₅ -H) |
| | 7.05-8.35, m | 12H | Ar-H |

CONTD. Table IV.3.

| 1 | 2 | 3 | 4 |
|---|-----------------------------|-----|--------------------------------------|
| 6a | 6.60, s | 1H | PyH (C ₅ -H) |
| | 6.75-7.95, m | 14H | Ar-H |
| b | 6.65, s | 1H | PyH (C ₅ -H) |
| | 2.50, s | 6H | di-CH ₃ |
| | 6.85-8.15, m | 12H | Ar-H |
| c | 6.70, s | 1H | PyH (C ₅ -H) |
| | 2.95, s | 12H | di N-(CH ₃) ₂ |
| | 6.85-8.15, m | 12H | Ar-H |
| d | 6.60, s | 1H | PyH (C ₅ -H) |
| | 3.95, s | 6H | di (OCH ₃) |
| | 6.90-8.35, m | 12H | Ar-H |
| e | 6.75, s | 1H | PyH (C ₅ -H) |
| | 7.05-8.35, m | 12H | Ar-H |
| f | 6.80, s | 1H | PyH (C ₅ -H) |
| | 7.15-8.45, m | 12H | Ar-H |
| g | 6.85, s | 1H | PyH (C ₅ -H) |
| | 7.10-8.35, m | 12H | Ar-H |
| h | 6.60, s | 1H | PyH (C ₅ -H) |
| | 3.85, d(J=6H _z) | 12H | di(3,4-di OCH ₃) |
| | 6.95-8.28, m | 10H | Ar-H |
| i | 6.70, s | 1H | PyH (C ₅ -H) |
| | 7.10-8.30, m | 12H | Ar-H |
| s = singlet m = multiplet d = doublet | | | |

CHAPTER V

CHAPTER-VSTUDIES ON METALLATION OF p - SUBSTITUTED PHENACYLIDENEDIMETHYL
SULFURANES : Hg(II), Cd(II), Co(II) AND Ni(II) COMPLEXES OF
AMBIDENTATE SULFURANES

V.1. ABSTRACT :

The synthesis of Hg(II), Cd(II), Co(II) and Ni(II) halides complexes with p-substituted dimethylsulfonium ylides are reported. The π -sulfuranes employed include phenacylidenedimethylsulfurane, p-fluorophenacylidenedimethylsulfurane, p-chlorophenacylidine-dimethylsulfurane, p-bromophenacylidenedimethylsulfurane, p-nitrophenacylidenedimethylsulfurane and m-nitrophenacylidene-dimethylsulfuranes. The presence of the sulfonium ions non coordinated counter ion was supported by IR spectral data. The $\nu(\text{C}=\text{O})$ frequencies of the complexes showed blue shift, relative to those of free S-ylides, approaching those of completely protonated 'Onium'salt, which indicates co-ordination via the methine carbon atom. The structures of the resulting complexes were elucidated on the basis of IR spectral data and elemental analysis.

V.2. INTRODUCTION :

Ylides are considered as versatile ligands for metals in their various oxidation states. They differ from other organic ligands in that the ylides co-ordinate to the metal ion as a neutral ligand to form a σ -bond between the ylide carbon and

the metal atom. The work on metallation of ylides was started in the right earnest from 1965¹. Previous to this, only preliminary studies on the reaction of inorganic components with ylides were reported². Various groups of workers have since been attracted more and more by many fascinating aspects of this newly emerging branch of organometallic chemistry. Later on many studies have been reported concerning the reaction of various ylides with boron, aluminium^{3,4}, mercury^{5,6} and tin compounds. However, there have been few reports on the reactions of ylide with transitional metals⁷⁻¹¹ and studies of metallate complexes containing co-ordinating ylide are also very rare to-date¹⁰⁻¹².

Recently, studies on the synthesis of metallate complexes by the reaction of pyridinium ylides with metal halides, has attracted a good deal of attention in the field of organometallic chemistry. Based on up-to-date information pyridinium ylides are supposed to hold a superior position among the other nitrogen ylides. Such studies though still in infancy, showed a great potentiality due to marked stability of the resulting ylide metallate complexes.

It is apparent that work in the field of metallation with S-ylide has begun. There is sure promise of great potential for the ylide metallate complexes are characterised by greater stability than their parent ylide. It is in this context that

it was thought worthwhile to extend this type of studies to prepare metallate complexes of some transitional metals viz. Hg(II), Cd(II), Co(II) and Ni(II) with some p-substituted phenacylidenedimethyl sulfonium ylide.

V.3. RESULTS AND DISCUSSION :

Reaction of dimethyl sulfide with phenacyl bromide, p-fluorophenacyl bromide, p-chlorophenacyl bromide, p-bromophenacyl bromide, p-nitrophenacyl bromide and m-nitrophenacyl bromide in benzene at reflux temperature, gave phenacyldimethylsulfonium bromide (1a), p-fluorophenacyldimethylsulfonium bromide (1b), p-chlorophenacyldimethylsulfonium bromide (1c), p-bromophenacyldimethylsulfonium bromide (1d), p-nitrophenacyldimethylsulfonium bromide (1e) and m-nitrophenacyldimethylsulfonium bromide (1f) respectively in fair to good yields. The structures of sulfonium salts (1a-f) were confirmed comparison of melting point of salt with those reported in literature and spectral data.

The IR spectra of salt (1a-f) showed a characteristic absorption band due to C=O stretching vibrations in the region $1670-1690\text{ cm}^{-1}$ for carbonyl group. The diagnostic absorption bands in the region $3300-3000\text{ cm}^{-1}$ were observed due to C-H stretching vibration of methylene groups attached to S-atom. The NMR spectra of salts (1a-f) showed a singlet at $\delta 3.00-3.15$ due to methyl protons directly attached to sulfonium group. A sharp singlet in the range $\delta 5.0-5.50$ exhibited methylene protons

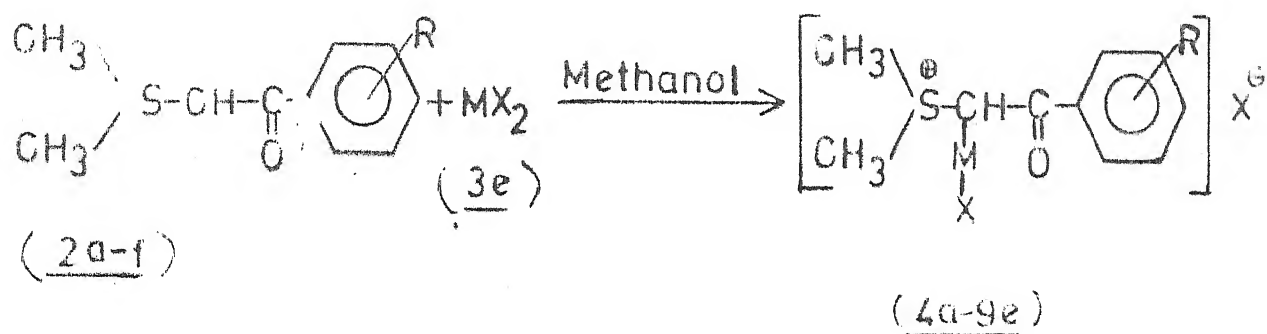
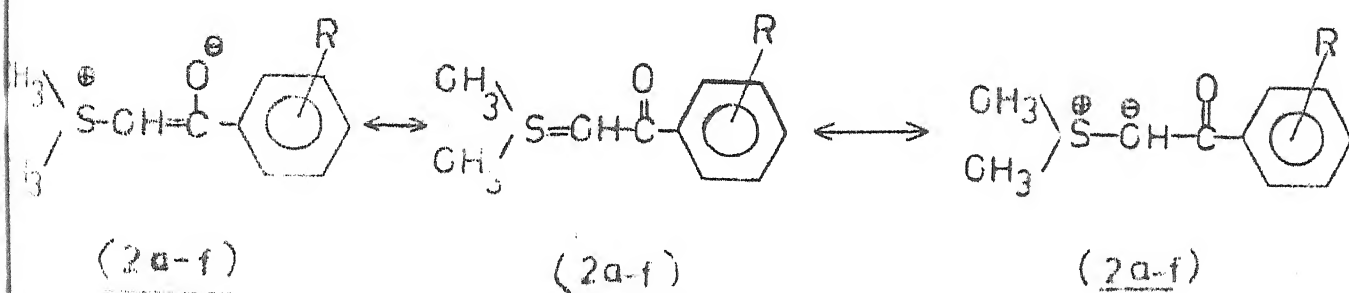
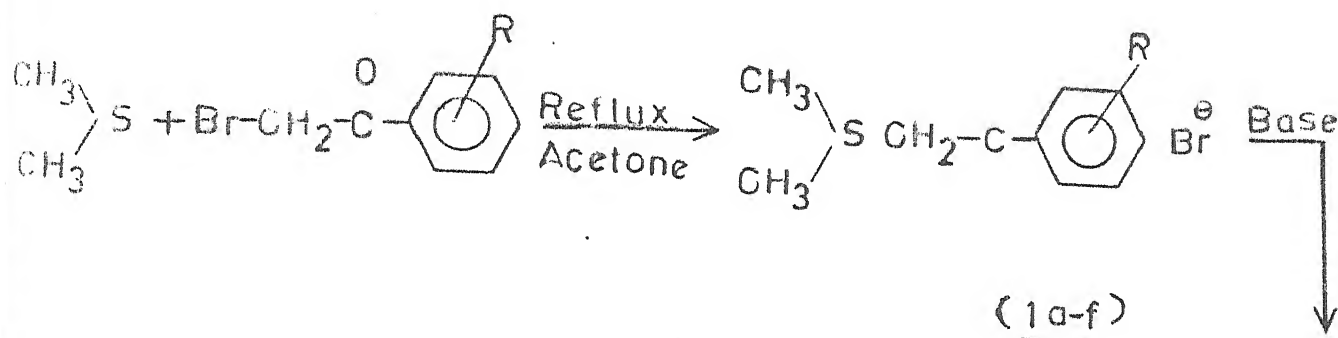
adjacent to sulfur group ($-\text{CH}_2-\text{S}^+ \text{ } \diagup \text{ } \diagdown$). The aromatic protons appeared in the range δ 7.20-8.35.

These salts (1a-f) on treatment with aq. NaOH generated a yellow coloration which was changed to orange colour clearly indicating the formation of ylides (2a-f) viz. phenacylidene-dimethyl sulfurane (2a), p-fluorophenacylidene-dimethyl sulfurane (2b), p-chlorophenacylidene-dimethyl sulfurane (2c), p-bromophenacylidene-dimethyl sulfurane (2d), p-nitrophenacylidene-dimethyl sulfurane (2e) and m-nitrophenacylidene-dimethyl sulfurane (2f) in good yields. These ylides (2a-f) were isolated in form of yellowish orange crystals (2a-f) were characterized on the basis of IR and NMR spectral data. The IR (KBr) spectral data showed a band of medium intensity in region $1500-1530\text{cm}^{-1}$ due to stretching vibration of C-O bond which is characteristic absorption of enolate structure. The NMR spectra showed a singlet at $3.05-3.20$ due to two methyl protons. A methine proton in ylides (2a-f) was absorbed at δ 4.25-4.35. The aromatic protons were exhibited in the region δ 7.20-8.15.

The ylide (2a-f) so generated, is isolable but can not be stored for a quite long time owing to its susceptibility towards atmospheric components and therefore the reaction of ylides was carried out in an atmosphere of nitrogen. The sulfonium salt (1a-f) are used in the reaction and ylides (2a-f) was generated in situ from its salts (1a-f).

The reaction of ylides (2a-f) with the halides of Hg(II), Cd(II), Co(II) and Ni(II) (MX_2 where M=metal, X=halogen) in methanol gave a series of metal halide complexes (4a-e, 9a-e) in 40-70% yields. The metal halide complexes $[M_2(\text{ylide})_2X_4]$ presumably contain a bridging X^{\ominus} group electron donating substituted (Cl, Br) having lone pair attached to phenyl ring of ylide counterpart of ylide (2b-d) increase the ease of formation of complex as evidenced by yield of final products (4-a).

The metallation reaction seems to proceed via intermediate ylide carbanion. The ylides used for the reactions may be represented by the three canonical structures (Scheme V.1). The value of carbonyl stretching vibrations observed for the ylides (4-9) showed an important contribution of enolate structure (III). In this structure of lone pair of electrons formally on the ylide carbanion is considered to be delocalised to a large extent. Thus, the ylides have two possible co-ordination sites towards the metal halide carbonyl oxygen which would result in low frequency shift of $\nu(C=O)$ owing increased enolate character. In general, the analytical data of the complexes were found to be in fairly good agreement with indicated formulations. But one can not rule out the presence of small amounts of the other salts which might be expected in view of high halide mobility likely to be encountered in these systems. Elemental analysis indicated that the complexes were 1:1 adducts probably dinuclear

Scheme.V.1

with halide bridging. The physical and spectral properties are included in table V.1 & V.2.

V.4. EXPERIMENTAL :

V.4.1. Starting Materials :

All the reagents were obtained from commercial sources (E.Merck, BDH, SISCO etc.). Starting materials were prepared according to the procedure reported in literature.

V.4.2. Preparation of p-substituted phenacyldimethylsulfonium bromide (1a-f):

General procedure :

A solution of 100m mole of p-substituted phenacyl bromide and 100m mole of dimethylsulfide in 100ml of anhydrous benzene or tetrahydrofuran, was boiled for 6-8hrs. The excess of the solvent was evaporated and petroleum ether was added to precipitate the salts (1a-f). which were, then recrystallized from chloroform, petroleum ether (1:2). This procedure was followed to prepare the following salts-

Phenacyldimethylsulfonium bromide (1a),
white crystalline solid, m.p. 138-140°C (Lit.¹³ m.p. 140°C),

IR (KBr) data, 1690 cm^{-1} ($\nu_{\text{C=O}}$)

NMR (CDCl_3) data (δ ppm) \downarrow 3.15 (s, 6H, di CH_3), 5.05 (s, 2H, $\text{CH}_2\text{-S}^+$)
7.10-8.30 (m, 5H, ArH).

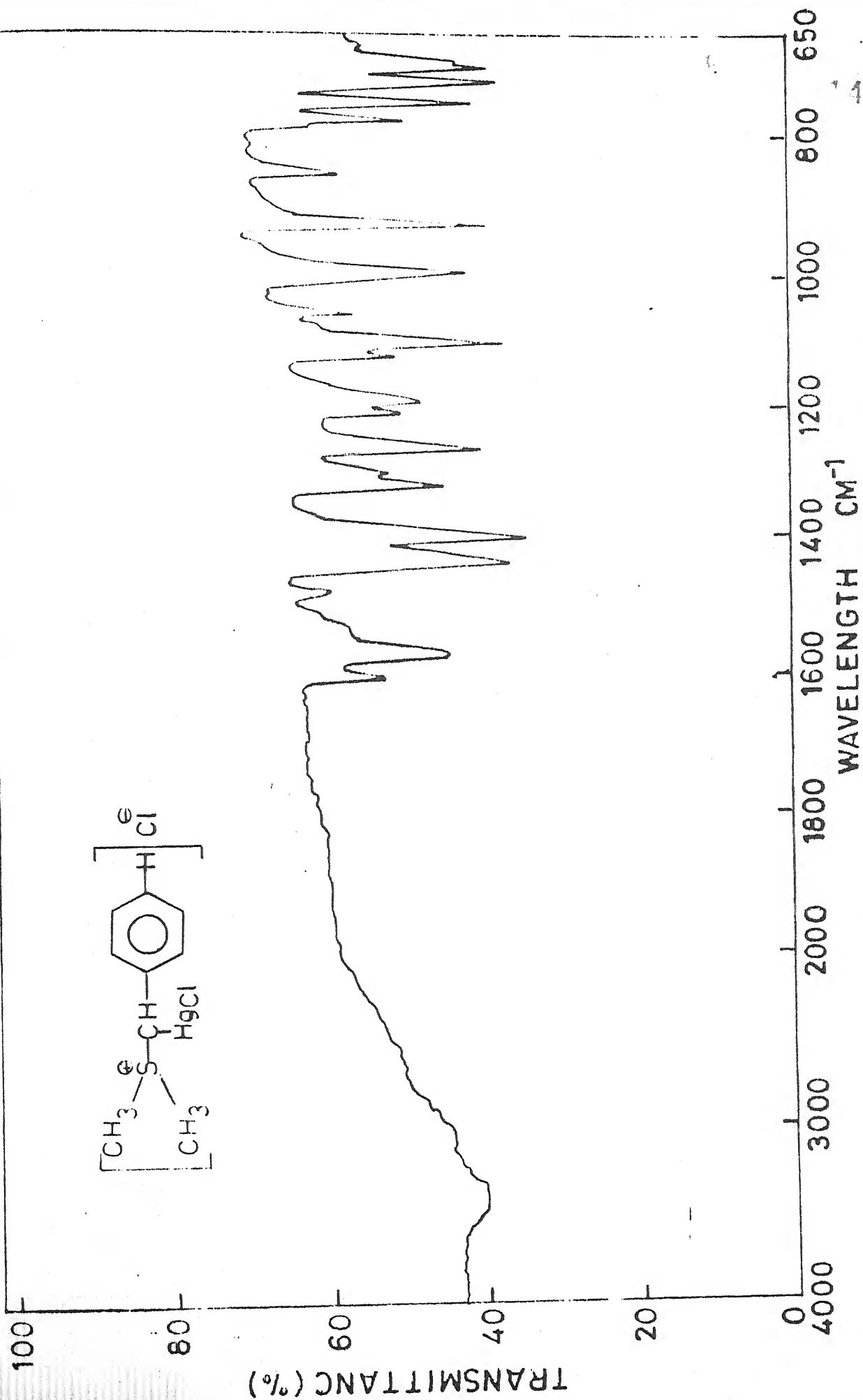


FIG. V.1 IR SPECTRUM OF COMPOUND (4a)

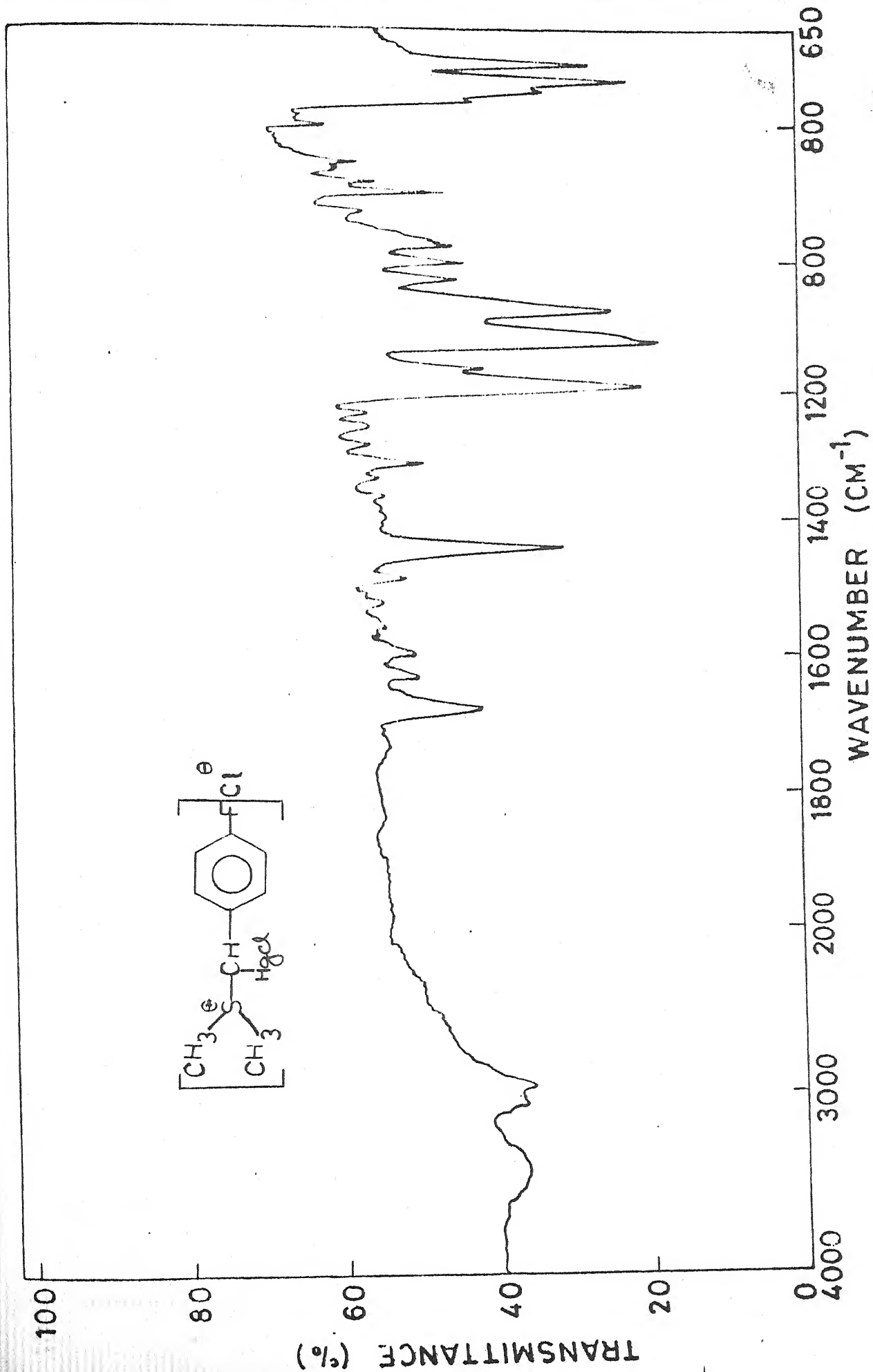


FIG. V.2 IR SPECTRUM OF SALT (5a)

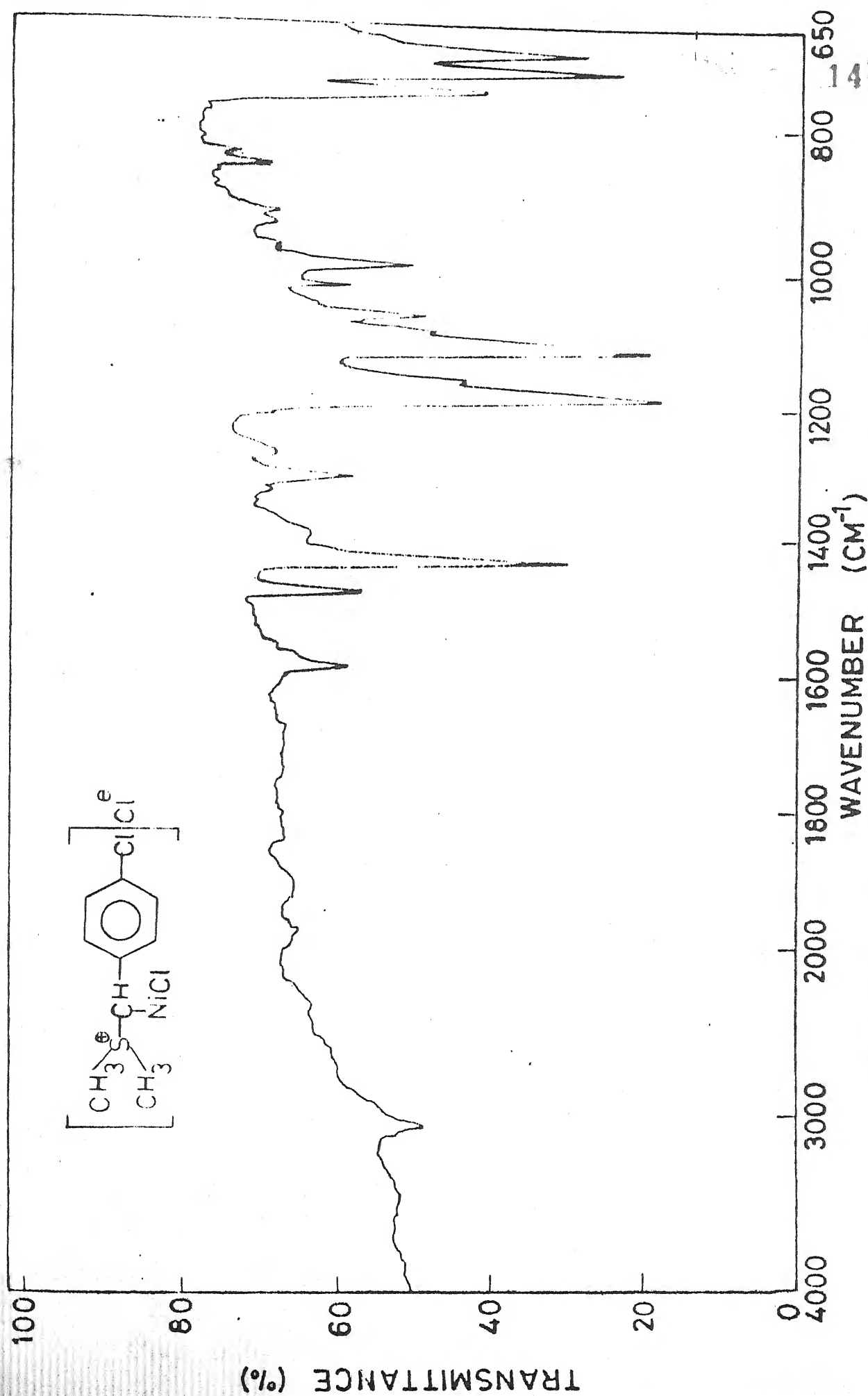


FIG. V.3 IR SPECTRUM OF COMPOUND (6a)

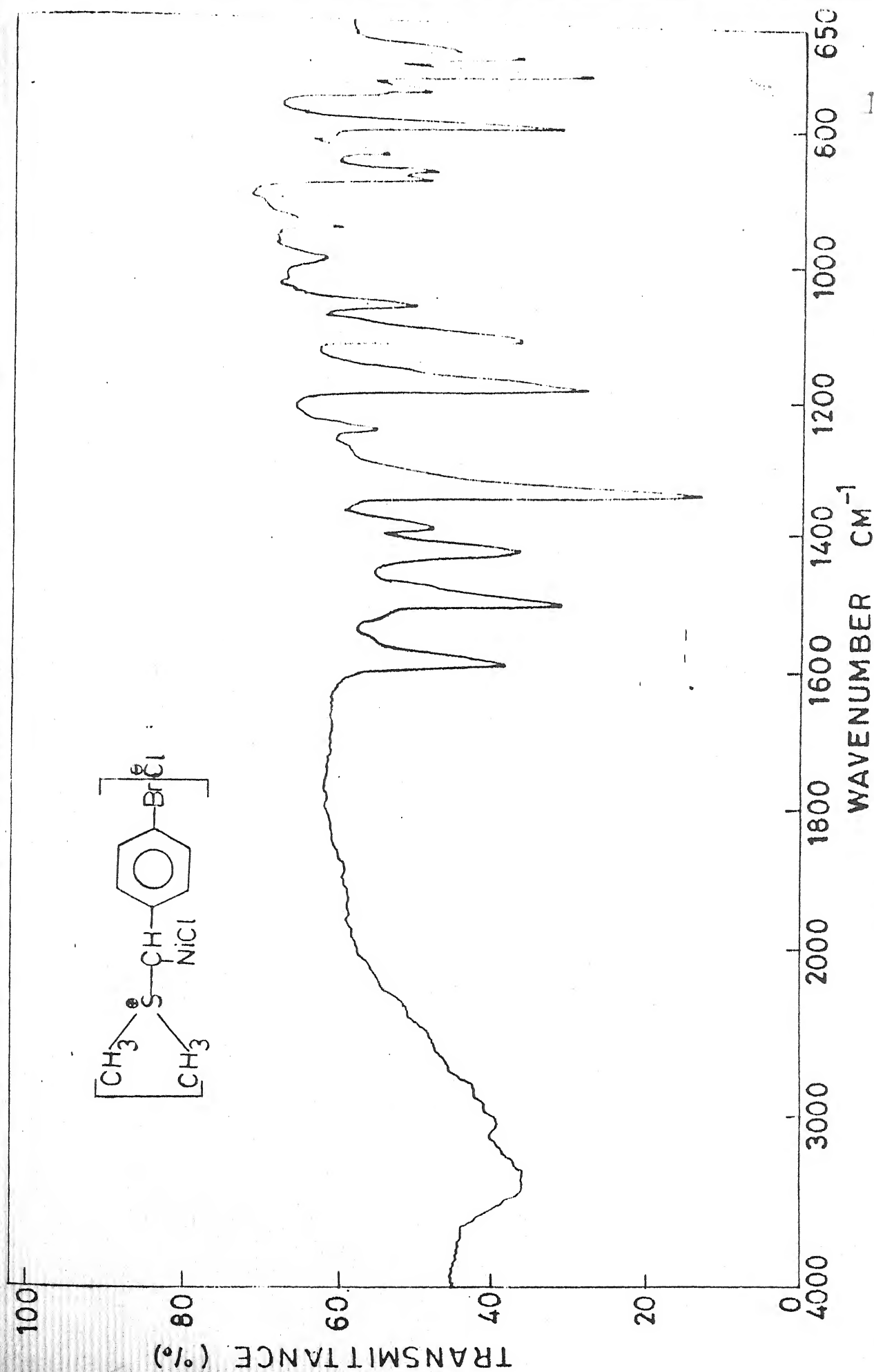


FIG. V.4 IR SPECTRUM OF COMPOUND (70a)

p-fluorophenacyldimethylsulfonium bromide(1b)
 white coloured, m.p.(142-144°C) (Lit.¹⁴ m.p.144-145°C)
 IR(KBr) data: 1675 cm^{-1} ($\nu_{\text{C=O}}$)
 NMR(CDCl_3) (δ ppm): 3.25(s, 6H, diCH_3); 5.40(s, 2H, CH_2);
 7.25-7.85(m, 4H, ArH).

p-chlorophenacyldimethylsulfonium bromide(1c)
 pale yellow crystals, m.p.120-122°C(Lit.¹⁵ m.p.120°C)
 IR(KBr) data: 1670 cm^{-1} ($\nu_{\text{C=O}}$)
 NMR(CDCl_3) data (δ ppm): 3.15(s, 6H, diCH_3); 5.25(s, 2H, $-\text{CH}_2-\text{S}^+\text{C}_6\text{H}_4-$);
 7.20-8.25(m, 4H, ArH).

p-bromophenacyldimethylsulfonium bromide (1d)
 yellow crystals, m.p.132-134°C(Lit.¹⁶ m.p.134°C)
 IR(KBr) data: 1685 cm^{-1} ($\nu_{\text{C=O}}$)
 NMR(CDCl_3) data (δ ppm): 3.20(s, 6H, diCH_3); 5.15(s, 2H, $\text{CH}_2-\text{S}^+\text{C}_6\text{H}_4-$);
 7.20-8.25(m, 4H, ArH).

p-nitrophenacyldimethylsulfonium bromide (1e)
 orange yellow crystals, m.p.150-152°C(Lit.¹⁷ m.p.152-154°C)
 IR(KBr) data: 1690 cm^{-1} ($\nu_{\text{C=O}}$)
 NMR(CDCl_3) data (δ ppm): 3.30(s, 6H, diCH_3); 5.35(s, 2H, $\text{CH}_2-\text{S}^+\text{C}_6\text{H}_4-$);
 7.25-8.40(m, 4H, ArH).

m-nitrophenacyldimethylsulfonium bromide(1f)
 orange(m.p.148-150°C) (Lit.¹⁸ m.p.150°C)
 IR(KBr) data: 1685 cm^{-1} ($\nu_{\text{C=O}}$)
 NMR(CDCl_3) data (δ ppm): 3.30(s, 6H, diCH_3); 5.10(s, 2H, CH_2);
 7.15-7.70(m, 4H, ArH).

V.4.3. Preparation of p-substituted phenacylidenedimethyl sulfurane (2a-f):

Taking the p-substituted phenacyldimethylsulfonium bromide (50m mole) was dissolved in water (30ml). The coloured suspension was filtered and the clear filtrate was treated with 10% Aq. NaOH (15ml). The solution was stirred for 6-8 hrs. and then extracted several times with CHCl_3 . The chloroform extract was dried with Na_2SO_4 and evaporated to give coloured oil which on cooling gave coloured solid. These coloured solids on crystallization with ethanol afforded light coloured crystals of p-substituted phenacylidene dimethyl sulfurane .

p-phenacylidenedimethylsulfurane (2a)

yellow crystals m.p. $70-72^\circ\text{C}$ (Lit. m.p. $74-76^\circ\text{C}$)

IR(KBr) data: 1690cm^{-1} ($\nu_{\text{C=O}}$)

NMR(CDCl_3) data (δ_{ppm}): 3.15(s, 6H, diCH_3), 5.05(s, 2H, $-\text{CH}-\text{S}^+ \text{<}$)
7.10-8.30(m, 5H, ArH) .

p-fluorophenacylidenedimethylsulfurane (2b)

light pale yellow crystals m.p. $66-68^\circ\text{C}$ (Lit. m.p. 66°C)

IR(KBr) data: 1530cm^{-1} ($\nu_{\text{C=O}}$)

NMR(CDCl_3) data (δ_{ppm}): 3.20(s, 6H, diCH_3); 4.35(s, 1H, $-\text{CH}-\text{S}^+ \text{<}$)
7.30-8.20(m, 4H, ArH) .

p-chlorophenacylidenedimethylsulfurane (2c)

light reddish yellow crystals, m.p. $80-82^\circ\text{C}$ (Lit. $78-80^\circ\text{C}$)

IR(KBr) data: 1520cm^{-1} ($\nu_{\text{C=O}}$)

NMR(CDCl₃) data (δ ppm) : 3.15(s, 6H, diCH₃) ; 4.20(s, 1H, CH-S⁺) ;
7.15-8.15(m, 4H, ArH) .

p-bromophenacylidenedimethylsulfurane(2d)

yellow shining ,m.p. 86-88°C(Lit. m.p.90-91°C)

IR(KBr) data: 1525Cm⁻¹ (ν C=O)

NMR(CDCl₃) data (δ ppm) : 3.10(s, 6H, diCH₃) ; 4.15(s, 1H, CH-S⁺) ;
7.20-8.20(m, 4H, ArH) .

p-nitrophenacylidenedimethylsulfurane(2e)

light reddish violet crystals, m.p.90-92°C(Lit. m.p.92-94°C)

IR(KBr) data: 1530Cm⁻¹ (ν C=O)

NMR(CDCl₃) data (δ ppm) : 3.30(s, 6H, diCH₃) ; 4.35(s, 1H, CH-S⁺) ;
7.25-8.25(m, 4H, ArH) .

m-nitrophenacylidenedimethylsulfurane(2f)

red violet crystals, m.p.98-100°C (Lit. m.p.96-98°C)

IR(KBr) data: 1525Cm⁻¹ (ν C=O)

NMR(CDCl₃) data (δ ppm) : 3.25(s, 6H, diCH₃) ; 4.30(s, 1H, CH-S⁺) ;
7.20-8.15(m, 4H, ArH) .

V.4.4. Synthesis of metal ylide complexes(4a-9e) :

General procedure :

A solution of metal halide (1.0m mole) in methanol (20ml) was added dropwise to the solution of substituted phenacylidenedimethylsulfonium ylide(2.0m mole) in methanol (20ml) . Immediately after the complete addition a precipitate

began to form rapidly. The mixture was stirred for further two hours at the room temperature and the solid was then filtered off, washed with methanol and diethyl ether and dried vacuo over calcium sulfate to afford titled complexes(4a-9e) in good yields.

REFERENCES

1. A.W. Jhonson, 'Ylide Chemistry', Academic Press, New York, N.Y. (1966).
2. D. Seyferth and S.O. Grim, J.Amer.Chem.Soc., 83, 1613(1961).
3. K.W. Musker and R.R. Stevens, Inorg.Chem., 8, 255(1969).
4. H. Schmidbaur and W. Tronich, Chem.Ber., 101, 595(1968).
5. D. Seyferth and S.O. Grim, J.Amer.Chem.Soc., 83, 1610(1961).
6. N.A. Nesmeyanov, V.M. Novikov and O.A. Reutov, J.Organomet. Chem., 4, 202(1965).
7. J.C. Ketz and D.G. Pedrotty, J.Organomet.Chem., 22, 425 (1970).
8. D. Cashman and F.J. Lalor, J.Organomet.Chem., 32, 351(1971)
9. K.A.O. Starzewski, H.T. Dieck, K.D. Frang and F. Hofmann, J.Organomet.Chem., 42, C35 (1972).
10. P.A. Arnup and M.C. Baird, Inorg.NaCl.Chem.Lect., 5, 65 (1969).
11. R.J. Sundberg, R.E. Shepherd and H. Taube, J. J.Amer. Chem.Soc., 94, 6558 (1972).
12. E.T. Welski, Jr., J.L. Silver, M.D. Jansson and J.L. Burmeister, J.Organomet.Chem., 102, 365-68 (1975).
13. A.W. Jhonson and R.T. Arnel, J.Org.Chem., 34, 1240(1969).

14. K.C. Gupta, P. Manglum, Curr.Sci., 58, 1196 (1989).
15. B.M. Trost, J.Amer.Chem.Soc., 89, 138 (1962).
16. F. Krohnke and K. Ellegast, Chem.Ber., 86, 1554 (1970).
17. K.W. Ratts and A.N. Rao, J.Org.Chem.31, 1185 (1966).
18. B.M. Trost, J.Amer.Chem.Soc., 89, 138 (1962).

TABLE V.1.: PHYSICAL PROPERTIES OF METAL YLIDE COMPLEXES (4a-9e).

| Comp- ound | M | X | R | m.p. °C | Yields % | Analysis found (Calcd.) % | | |
|---------------|----|----|-----|------------|-------------|---------------------------|----------------|------------------|
| | | | | | | C | H | X = Cl, Br, F |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 4a | Hg | Cl | H | 190-92 | 40 | 26.50 (26.54) | 2.69 (2.65) | 15.91 (15.71) |
| b | Hg | Br | H | 185-87 | 50 | 25.90 (25.92) | 2.54 (2.59) | 17.37 (17.35) |
| c | Cd | Cl | H | 198-20 | 45 | 19.51 (19.56) | 3.34 (3.31) | 19.48 (19.50) |
| d | Ni | Cl | H | 170-72 | 50 | 38.98 (38.96) | 3.86 (3.89) | 23.07 (23.05) |
| e | Co | Cl | H | 180-82 | 45 | 38.69 (38.71) | 3.86 (3.87) | 22.92 (22.90) |
| 5a | Hg | Cl | 4-F | 205-08 | 50 | 25.50 (25.53) | 2.35 (2.34) | 15.12 (15.11) |
| b | Hg | Br | 4-F | 188-90 | 45 | 21.49 (21.47) | 1.98 (1.96) | 28.64 (28.62) |
| c | Cd | Cl | 4-F | 168-70 | 48 | 31.46 (31.49) | 2.88 (2.89) | 18.62 (18.64) |
| d | Ni | Cl | 4-F | 180-82 | 50 | 36.84 (36.81) | 3.35 (3.37) | 21.79 (21.78) |
| e | Co | Cl | 4-F | 178-80 | 55 | 36.56 (36.59) | 3.37 (3.35) | 21.67 (21.65) |

Contd. Table V.1.

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|----|----|----|-------------------|--------|----|------------------|----------------|------------------|
| 6a | Hg | Cl | 4-Cl | 190-92 | 65 | 24.65 (24.67) | 2.23 (2.26) | 21.86 (21.89) |
| b | Hg | Br | 4-Cl | 180-82 | 65 | 32.02 (32.04) | 2.93 (2.94) | 9.49 (9.48) |
| c | Cd | Cl | 4-Cl | 166-68 | 55 | 30.22 (30.19) | 3.63 (3.65) | 26.80 (26.79) |
| d | Ni | Cl | 4-Cl | 172-74 | 60 | 35.06 (35.04) | 3.22 (3.20) | 31.06 (31.09) |
| e | Co | Cl | 4-Cl | 164-66 | 58 | 34.82 (34.83) | 3.20 (3.19) | 30.92 (30.91) |
| 7a | Hg | Cl | 4-Br | 180-82 | 60 | 21.75 (21.78) | 1.92 (1.99) | 12.87 (12.89) |
| b | Hg | Br | 4-Br | 170-72 | 55 | 19.37 (19.35) | 1.75 (1.77) | 2.56 (2.58) |
| c | Cd | Cl | 4-Br | 202-04 | 50 | 27.10 (27.11) | 2.48 (2.49) | 16.04 (16.06) |
| d | Ni | Cl | 4-Br | 210-12 | 45 | 30.82 (30.85) | 2.81 (2.84) | 18.35 (18.35) |
| e | Co | Cl | 4-Br | 178-80 | 50 | 30.86 (30.84) | 2.80 (2.83) | 18.23 (18.25) |
| 8a | Hg | Cl | 4-NO ₂ | 164-66 | 40 | 24.13 (24.14) | 2.23 (2.21) | 14.30 (14.29) |
| b | Hg | Br | 4-NO ₂ | 186-88 | 45 | 23.70 (23.72) | 2.15 (2.17) | 15.79 (15.81) |

Contd. Table V.1.

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|----|----|----|-------------------|--------|----|------------------|----------------|------------------|
| c | Cd | Cl | 4-NO ₂ | 198-20 | 50 | 20.39 (20.41) | 2.67 (2.69) | 17.42 (17.40) |
| d | Ni | Cl | 4-NO ₂ | 190-92 | 40 | 33.97 (33.99) | 3.14 (3.12) | 20.14 (20.11) |
| e | Co | Cl | 4-NO ₂ | 180-82 | 45 | 33.89 (33.80) | 3.07 (3.09) | 20.13 (20.11) |
| 9a | Hg | Cl | 3-NO ₂ | 180-82 | 50 | 24.25 (24.14) | 2.10 (2.21) | 4.35 (4.29) |
| b | Hg | Br | 3-NO ₂ | 192-94 | 45 | 23.86 (23.72) | 2.12 (2.17) | 15.74 (15.81) |
| d | Cd | Cl | 3-NO ₂ | 178-80 | 55 | 20.50 (20.41) | 2.61 (2.69) | 17.51 (17.40) |
| d | Ni | Cl | 3-NO ₂ | 200-02 | 40 | 33.88 (33.99) | 3.19 (3.12) | 20.18 (20.11) |
| e | Co | Cl | 3-NO ₂ | 196-98 | 45 | 33.75 (33.80) | 3.15 (3.09) | 20.22 (20.11) |

TABLE V.2: IR SPECTRAL DATA FOR METAL COMPLEXES.
(4a-9e)

| Compound | IR Data (KBr) (Cm ⁻¹) | | | |
|----------|-----------------------------------|-----------|-----------|-----------------------|
| | ν C-H | ν C=O | ν C-M | ν NO ₂ |
| 4a | 3405 | 1650 | 730 | |
| b | 3380 | 1680 | 725 | |
| c | 3370 | 1668 | 715 | |
| d | 3285 | 1645 | 740 | |
| e | 3400 | 1640 | 730 | |
| 5a | 3490 | 1630 | 710 | |
| b | 3420 | 1665 | 735 | |
| c | 3405 | 1650 | 715 | |
| d | 3385 | 1660 | 728 | |
| e | 3408 | 1655 | 730 | |
| 6a | 3400 | 1640 | 738 | |
| b | 3415 | 1675 | 730 | |
| c | 3408 | 1680 | 738 | |
| d | 3420 | 1666 | 722 | |
| e | 3410 | 1684 | 732 | |
| 7a | 3428 | 1670 | 718 | |
| b | 3408 | 1668 | 728 | |
| c | 3398 | 1650 | 708 | |
| d | 3410 | 1645 | 715 | |
| e | 3402 | 1650 | 710 | |
| 8a | 3420 | 1645 | 718 | 1338, 1520 |
| b | 3415 | 1668 | 728 | 1320, 1515 |
| c | 3430 | 1675 | 720 | 1335, 1525 |
| d | 3408 | 1667 | 730 | 1330, 1535 |
| e | 3415 | 1655 | 720 | 1338, 1540 |

CONTD. TABLE V.2.

| Compound | IR Data (KBr) (Cm ⁻¹) | | | |
|----------|-----------------------------------|-----------|-----------|-----------------------|
| | ν C-H | ν C=O | ν C-M | ν NO ₂ |
| 9a | 3415 | 1668 | 735 | 1320, 1540 |
| b | 3395 | 1655 | 728 | 1328, 1538 |
| c | 3405 | 1666 | 735 | 1335, 1548 |
| d | 3428 | 1665 | 745 | 1330, 1540 |
| e | 3420 | 1675 | 730 | 1338, 1545 |

ν = Stretching vibrations.